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Vol. 17, No. 4 October 1936

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RESEARCH PAPER RP925

Part of Journal of Research of the National Bureau of Standards, Volume 17, October 1936

HARMONIC METHOD OF INTERCOMPARING THE OSCILLATORS OF THE NATIONAL STANDARD OF RADIO FREQUENCY

By Evan G. Lapham

ABSTRACT

A method of precisely measuring the frequency difference between two frequency standards which have nominally the same fundamental frequency is outlined. The application of this method to the continuous intercomparison of the piezo oscillators in the primary frequency standard maintained by the National Bureau of Standards is described.

The customary method of measuring the frequency difference between two piezo oscillators utilizes the beat frequency between the two standards at the fundamental frequency or one of the harmonics. The method described utilizes the frequency produced by heterodyning two consecutive harmonics to obtain any desired precision of frequency comparison without necessitating the operation of any circuits at exceedingly high frequencies.

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I. INTRODUCTION

The primary frequency standard maintained by the National Bureau of Standards is described in a previous paper.[1] As described in that paper, the output frequencies of the individual piezo oscillators, which together constitute the primary frequency standard, are continuously measured in terms of the frequency of one of the oscillators as a reference standard. This measurement has hitherto been made by heterodyning the output of each of the standards with the output of the reference standard, and recording graphically the frequency difference. The range of the recorder was from 0 to 0.4 cycle per second. Since the measurement was made at the fundamental frequency, 100 kilocycles per second, 0.4 cycle per second corresponded to a change in the frequency of the standard of 4 parts per million. There are 100 divisions on the recorder paper, so that, other conditions being constant, the changes of the frequency difference could be read to ± 2 parts per 100 million.

The precision of this method of intercomparison was adequate at the time the standard was originally installed. The frequency variations were of such a magnitude that better precision was unnecessary.

[1] Hall, Heaton, and Lapham. *The National Primary Standard of Radio Frequency*, J. Research NBS 14, 85 (1935) RP759.

In the course of time, however, the variations of frequency were reduced considerably, with the result that the record obtained with this arrangement was practically a straight line. It showed the gradual changes in the frequency differences over a period of a few days, but did not resolve the random variations of small magnitude which take place during shorter time intervals, such as an hour or a few hours.

The simplest method of increasing the precision of the recorder was to measure the beat frequency at a harmonic of the fundamental frequency. If the reference standard has a frequency F, and a standard to be compared with it has a frequency $F \pm f$, the frequency difference is f cycles per second. Multiplying both standards by a factor n, the frequency difference is given by

$$n(F \pm f) - nF = nf.$$

The precision of the measurement is multiplied by a factor equal to the harmonic number if the accuracy of the recording equipment remains the same. This condition can be realized if the frequencies of the different standards are sufficiently close to one another that the range of beat frequency to be recorded is unchanged.

A consideration in the choice of methods was the desirability of making maximum use of the existing equipment. This included 100-kilocycle mixing circuits which produced the beat frequency to operate the recorder. In order not to discard those circuits it was necessary to use a method which produces the beat-frequency difference for the harmonic frequencies by mixing appropriate 100-kilocycle outputs.

II. METHOD

The method utilizes the frequency difference between two successive harmonics of the fundamental frequency. If the frequency of any standard is multiplied by a factor n, and the frequency of the reference standard is multiplied by a factor $(n-1)$, the frequency difference is given by

$$n(F \pm f) - (n-1)F = nF \pm nf - nF + F = F \pm nf.$$

This intermediate frequency differs from the fundamental frequency of the reference oscillator by an amount equal to n times the frequency difference between the two standards at their fundamental frequency or nf. If this process is repeated, multiplying the above intermediate frequency by the factor n, and subtracting from it the fundamental frequency of the reference standard, multiplied by the factor $(n-1)$, a new intermediate frequency is obtained, and is equal to

$$n(F \pm nf) - (n-1)F = nF \pm n^2 f - nF + F = F \pm n^2 f.$$

The intermediate frequency now differs from the fundamental frequency of the reference standard by a factor $n^2 f$. This process of multiplication can be repeated until the frequency difference is of any desired magnitude.

The above arrangement as applied to the intercomparison of the oscillators of the primary standard is shown schematically for a single unit in figure 1. The frequency of the reference standard is multiplied by 9 by means of a harmonic amplifier. If the fundamental frequency of the reference standard is 99,999.98 cycles per second, the output of the frequency multiplier will have a frequency of 899,999.82 ($9 \times 99{,}999.98$) cycles per second. In a similar manner,

the frequency of the standard to be compared with the reference standard is multiplied by 10, which gives an output of 1,000,000.00 (10×100,000.00) cycles per second if this standard has a fundamental frequency of exactly 100,000.00 cycles per second. Combining these two outputs in a detector-circuit arrangement a difference frequency is produced which is nominally 100,000 cycles per second and in the illustrative example is exactly 100,000.18 cycles per second. This 100-kilocycle output is amplified and coupled, along with the output of the reference standard, into the mixing circuits provided in the old arrangement. The difference frequency so produced is recorded just as in the old method. The beat frequency would be 0.20 cycle per second (100,000.18—99,999.98), which is exactly 10 times the beat frequency at the fundamental. The result is that the recorder indicates the frequency changes on the 10th harmonic, 1,000 kc/s. If a higher order of precision is desired, this process can be repeated, using the 100-kilocycle output of the detector amplifier as the input to the succeeding multiplier.

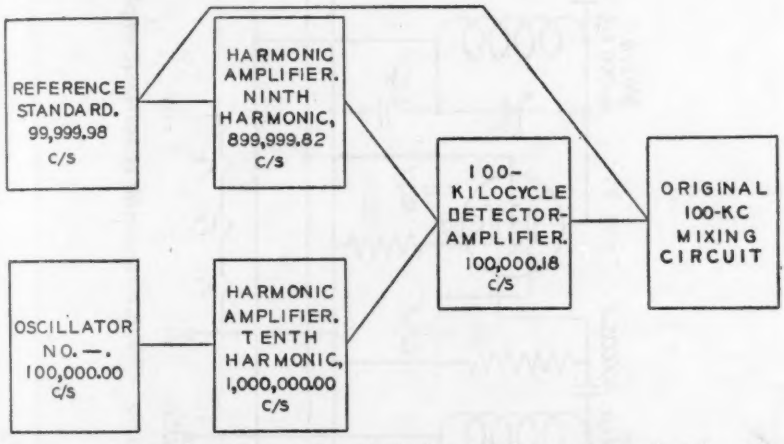
REFERENCE STANDARD. 99,999.98 C/S
HARMONIC AMPLIFIER. NINTH HARMONIC, 899,999.82 C/S
100-KILOCYCLE DETECTOR-AMPLIFIER. 100,000.18 C/S
ORIGINAL 100-KC MIXING CIRCUIT
OSCILLATOR NO.—. 100,000.00 C/S
HARMONIC AMPLIFIER. TENTH HARMONIC, 1,000,000.00 C/S

FIGURE 1.—*Schematic diagram of method of comparing a standard with reference standard.*

The equipment for the intercomparison of the entire group of standards consists of a frequency multiplier for the reference standard, to change its frequency from 100 to 900 kc/s a frequency multiplier for each of the standards to be recorded to change their frequency from 100 to 1,000 kc/s, a detector-amplifier for each standard, and the present intercomparison equipment.

III. CIRCUIT ARRANGEMENT

The harmonic-amplifier circuit arrangement is shown in figure 2. Two types of harmonic amplifiers are used as frequency multipliers, the one providing a 9-to-1 and the other a 10-to-1 multiplication. In the frequency multipliers the plate circuits of the multiplier stages are tuned to the desired harmonic. The tuned circuits must be low-loss circuits in order to reduce the troublesome effect of amplitude modulation at the input frequency. The multiplier stages are followed by an output amplifier which provides the necessary power

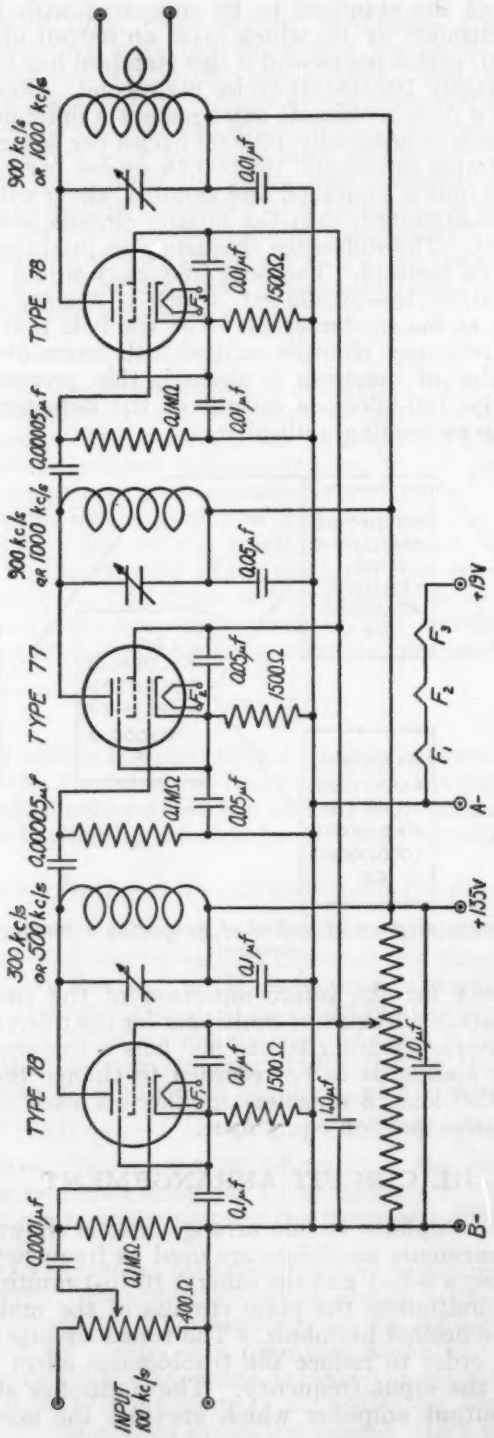

FIGURE 2.—*Circuit arrangement of harmonic amplifiers.*

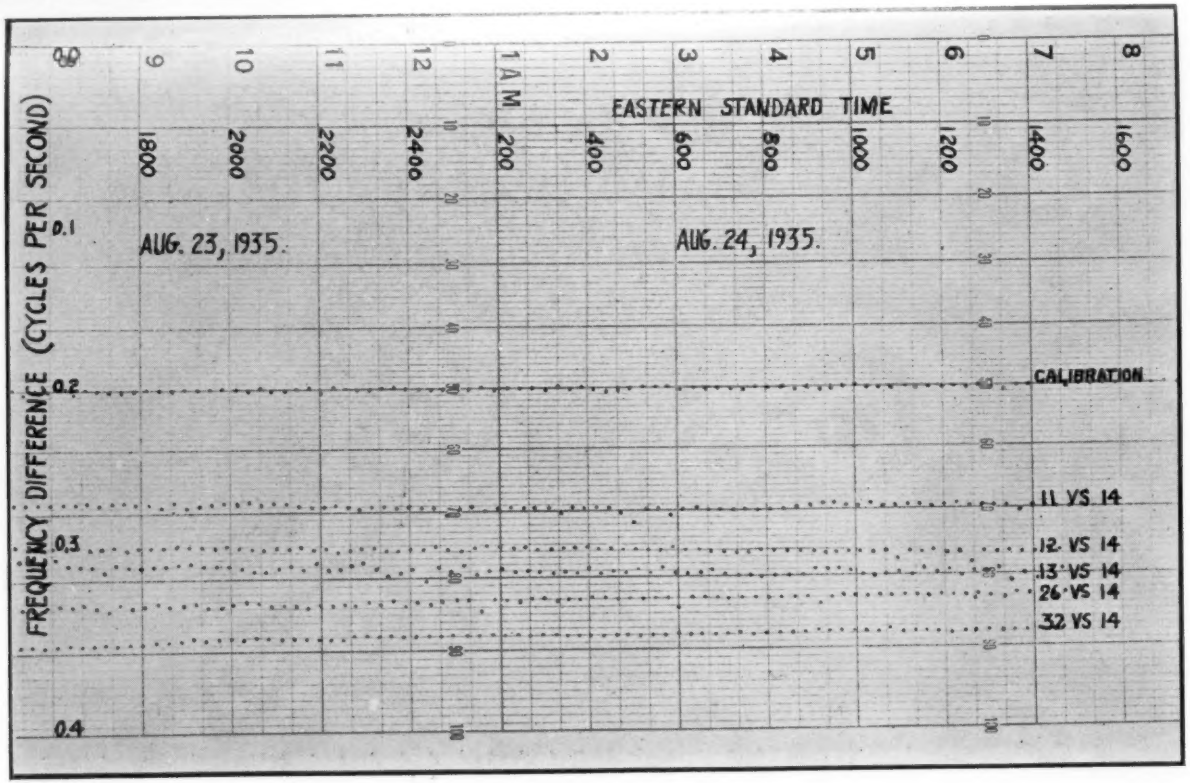

FIGURE 4.—*Sample record of beat frequency at fundamental frequency.*

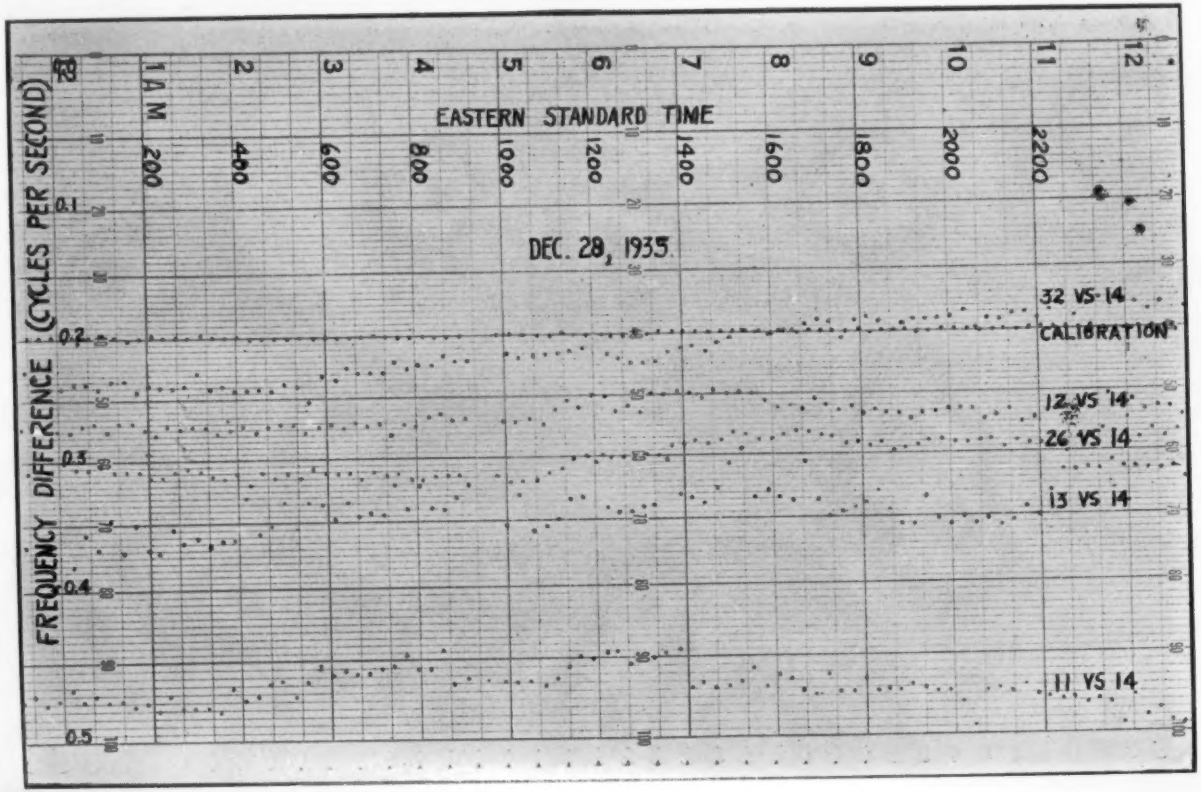

FIGURE 5.—*Sample record of beat frequency at tenth harmonic.*

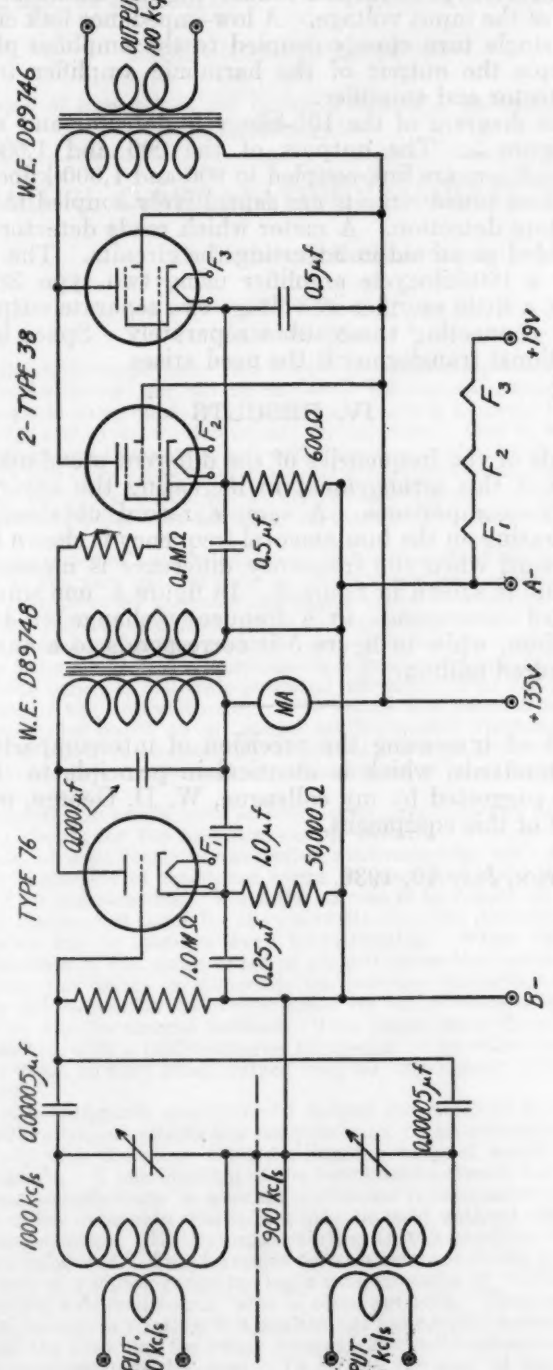

FIGURE 3.—*Circuit arrangement of 100-kilocycle detector-amplifier.*

output and also serves to further reduce the amplitude of undesired components of the input voltage. A low-impedance link circuit, consisting of a single turn closely coupled to the amplifier plate coil, is used to couple the output of the harmonic amplifier to the 100-kilocycle detector and amplifier.

The circuit diagram of the 100-kilocycle detector and amplifier is shown in figure 3. The outputs of the 900 and 1,000-kilocycle harmonic amplifiers are link-coupled to 900 and 1,000-kilocycle tuned circuits. These tuned circuits are capacitively coupled to a detector biased for plate detection. A meter which reads detector-plate current is provided as an aid in adjusting the circuits. The detector is followed by a 100-kilocycle amplifier using two type 38 tubes in parallel. At a little sacrifice in voltage two separate outputs can be obtained by connecting these tubes separately. Space is provided for the additional transformer if the need arises.

IV. RESULTS

The records of the frequencies of the different standards show the effectiveness of this arrangement in increasing the accuracy of the frequency intercomparisons. A sample record obtained with the recorder operating on the fundamental frequency is shown in figure 4. A similar record when the frequency difference is measured on the 10th harmonic is shown in figure 5. In figure 4, one small division on the record corresponds to a frequency change of 4 parts per hundred million, while in figure 5 it corresponds to a change of 0.5 part per hundred million.

A method of increasing the precision of intercomparison of two frequency standards, which is identical in principle to the one described, was suggested by my colleague, W. D. George, prior to the development of this equipment.

WASHINGTON, July 10, 1936.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP926

Part of Journal of Research of the National Bureau of Standards, Volume 17, October 1936

TEMPERATURE COMPENSATION OF MILLIVOLTMETERS

By Herbert B. Brooks

ABSTRACT

The formulas hitherto published for the temperature compensation of millivoltmeters by the Swinburne method are inexact. Furthermore, their sole objective being temperature compensation, they are capable of a multiply infinite number of solutions for any given millivoltmeter "mechanism"; that is, the permanent-magnet structure and the moving coil with its springs and pointer. Even if these formulas were free from error, their too-great generality imposes upon the instrument designer an impracticable amount of cut-and-try work to obtain a solution which takes care of other very necessary features besides temperature compensation.

Merely as a matter of academic interest, this paper gives the exact solution of the problem in the very general form in which it has been attacked by previous writers. It then presents the most practically useful of a number of other exact solutions which have been derived for various combinations of the three requirements other than temperature compensation. This most useful solution gives the relations to be satisfied in a temperature-compensated millivoltmeter which is to have definite values of full-scale potential difference, total damping resistance, and resistance of the millivoltmeter. The use of this solution is illustrated by numerical examples based on an actual millivoltmeter mechanism. The new formulas which relate to temperature compensation with any two, and with any one of these other three important requirements are of lesser importance and are given in outline only.

Millivoltmeters are rarely used as such, their preponderant use being in connection with shunts for the measurement of current. The combination, in the usual manner, of a perfectly compensated millivoltmeter with a shunt of zero temperature coefficient of resistance forms an ammeter which is not perfectly compensated for temperature. When the current to be measured is large in comparison with the current taken by the millivoltmeter, the defect in compensation as an ammeter will be small or even inappreciable. When the current to be measured becomes of the same order of magnitude as the current taken by the millivoltmeter, the defect in compensation becomes important. This is true, whether the millivoltmeter be compensated by the method of simple series resistance or by the Swinburne method. This paper presents a theorem which makes it possible, with a millivoltmeter compensated by either method, to measure currents down to very small values with no impairment of the temperature compensation.

The use of a manganin multiplier to extend the range of a Swinburne-compensated millivoltmeter affects the compensation by an amount which increases asymptotically with the range toward a limiting value of about 0.2 percent per degree centigrade. A modification of the Swinburne network has long been used by a German manufacturer to give an additional compensated higher range (3 volts) with which manganin multipliers may be used without affecting the temperature compensation. No formulas relating to this modified network appear to have been published. Two formulas for this case are given, the first of which covers the case of a higher range having a random value of "ohms per volt" and the other having a desired round value of ohms per volt. Their use is illustrated by numerical examples relating to a multirange instrument actually constructed.

The use of the formulas for every compensated millivoltmeter manufactured would add undesirably to the cost. To reduce the cost of compensation to a minimum, simple experimental procedures for factory use are outlined by which

millivoltmeters of a given type may be compensated rapidly and accurately if some previous experience has been had with the type in temperature compensation with the aid of the formulas.

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I. INTRODUCTION

A millivoltmeter is a voltmeter of such low range that the millivolt is the convenient unit for use in marking its scale. Millivoltmeters for direct current are usually made with full-scale values up to 750 millivolts. Similar instruments with full-scale values of 1 volt and above are usually called voltmeters and have their scales marked in volts. Millivoltmeters are used to only a limited extent for the measurement of potential differences, such as those in bolted contacts or switch contacts, or between adjacent commutator bars in the testing of armatures. For such measurements high accuracy is not required, consequently the effect of change of ambient temperature on the indications is usually not important.

By far the most important use of the millivoltmeter, however, is in connection with shunts for the measurement of currents. The range of such measurements is very wide, namely, from a small fraction of an ampere up to thousands of amperes. When a millivoltmeter is so used with a shunt, the propriety of calling it a "millivoltmeter" may be challenged, especially when its scale is marked in amperes. In such a case, the combination of millivoltmeter, leads, and shunt is effectively an ammeter. If the shunt (or a group of shunts) is built into the instrument and the scale is marked in amperes, the combination is always called an ammeter. However, when the shunts are external accessories, and the scale is marked in millivolts, the apparatus is usually called a "millivoltmeter with external shunts."

II. EFFECTS OF A CHANGE IN TEMPERATURE

For many measurements of direct current it is important that the accuracy shall not be appreciably affected by ordinary variations of the ambient temperature. The power loss in the windings of a millivoltmeter is so small that the temperature rise from this source is negligible. The practical requirement that a millivoltmeter shall give full-scale deflection for a relatively small potential difference between its terminals tends toward a construction which gives a relatively large change in the indication of the instrument as the ambient temperature varies. The net effect on the indication of a change in ambient temperature is the resultant of a number of changes, some of which tend to annul each other, and others, such as those caused by change of dimensions of the parts of the instrument, produce inappreciable effects on the indication.

In a permanent-magnet moving-coil instrument an increase of temperature of 1° C reduces the strength of the spring approximately 0.04 percent and reduces the magnetic flux density in the air gap about 0.02 percent. The weakening of the spring tends to increase the

deflection for a given current in the coil, and the lowering of the flux density tends to decrease the deflection; the net effect, in the average instrument, of a change of 1° C is thus to increase the deflection about 0.02 percent. The moving coil is usually of copper, sometimes of aluminum, and in either case its resistance increases about 0.4 percent for an increase of temperature of 1° C. If the small voltage to be measured could be applied directly to the coil, the reading of the instrument would thus decrease by 0.40−0.02=0.38 percent for a temperature rise of 1° C. This high value of temperature coefficient of the indication would be prohibitive for most purposes. With the facilities now available it is a simple matter to effect "temperature compensation" in a voltmeter of any range from a few volts up to any desired value. In a millivoltmeter, however, the desirability of minimizing the full-scale potential difference at the instrument terminals has made the problem somewhat difficult.

III. METHODS FOR EFFECTING TEMPERATURE COMPENSATION

1. COMPENSATION OF A MILLIVOLTMETER USED AS SUCH

It is possible to effect complete compensation of the average millivoltmeter by adding to the copper coil a series resistor of manganin [1] wire having a resistance of about 19 times that of the copper coil. This reduces the temperature coefficient of resistance of the instrument to one-twentieth of that of copper, and with a constant potential difference at the instrument terminals the decrease of current through the instrument as the temperature increases just balances the tendency, in the average instrument, toward increased deflection because of changes in the magnetic field and in the strength of the springs. As compared with the more complicated method of compensation which forms the principal subject of study in this paper, this method of compensation merely by the use of series resistance would be preferable because of its simplicity if it were not for one serious disadvantage, namely, the relatively high value of full-scale potential difference which is necessary if the instrument mechanism is to be sufficiently strong and the time for the pointer to come to rest is not to be too long. If these two requirements are to be satisfied, it is necessary to have a full-scale potential difference of say 100 to 200 millivolts. In switchboard instruments, and in portable instruments of medium grade for purposes not requiring the highest accuracy, the full-scale potential difference may be kept down by using only enough series resistance of manganin wire to get a partial compensation adequate for the purpose. Shunts having a drop of 50 millivolts with rated current may be used with such instruments. For portable instruments of precision grade a relatively high degree of temperature compensation is necessary, and when instruments of this grade, with a suitable relation between the full-scale torque and the weight of the moving element, are compensated merely by the use of series resistance, the full-scale potential difference of the instrument is too large to permit the use of 50-millivolt shunts.

Another method of compensating millivoltmeters avoids the difficulty of an excessive value of potential difference for full-scale deflec-

[1] The word "manganin" is used in this paper as a brief substitute for the inconveniently long expression "material of negligibly small temperature coefficient of resistance."

tion. It is based on the early work of Swinburne [2] in the temperature compensation of electrical instruments, and although he did not apply the method specifically to millivoltmeters it will be called the Swinburne method in this paper. It is illustrated by the diagram of figure 1. A manganin coil a'' is connected in series with the moving coil a'; a coil b of relatively large temperature coefficient β is connected in parallel with the two, and a coil c, usually and preferably of manganin wire, is connected as shown. The symbols a', a'', b, and c denote the various coils and also their resistances without reference to any particular temperature. The symbol a' refers to the moving coil and its springs and the sum of a' and a'' is denoted by a. The temperature coefficient α of the branch a is less than that of the copper or aluminum wire of the moving coil, partly because the series resistor a'' is made wholly or partly of manganin, and also because the temperature coefficient of resistance of the alloy springs is less than that of the wire of the coil. If the proper relations exist between the resistances and the temperature coefficients of the three branches a, b, and c of this network, the millivoltmeter will give the same indication, for a given applied voltage, at a chosen reference temperature and at a chosen other temperature. Between these temperatures the indication will go through a maximum value slightly greater than the indication at the chosen temperatures. If the values of resistance and temperature coefficient are properly chosen, the potential difference at the millivoltmeter terminals for full-scale deflection may be made less than 5 times the potential difference at the ends of the moving coil itself, as contrasted with 20 times for the simple series method of compensation. The Swinburne method makes it possible to obtain accurate temperature compensation in millivoltmeters of good torque-weight characteristic requiring only 50 millivolts for full-scale deflection. This advantage is secured at the cost of slightly greater complexity of the millivoltmeter network. A special limitation of the Swinburne-compensated millivoltmeter is that it has a relatively large temperature error if it be used either as an unshunted milliammeter or with a multiplier to increase its range as a millivoltmeter.

2. COMPENSATION OF A MILLIVOLTMETER USED WITH A SHUNT AS AN AMMETER

When a current is to be measured with a millivoltmeter connected to an external shunt it is necessary to assume that the shunt and the millivoltmeter may be at appreciably different temperatures because of either difference of environment or the temperature rise of the shunt under load. It follows that the resistance of the external shunt should not vary appreciably with temperature. If the shunt is mounted within the millivoltmeter and in sufficiently intimate thermal proximity to the moving coil, and the current to be measured is so small that the shunt and the moving coil have closely equal temperatures under all conditions, it is not necessary either that the shunt should have a zero temperature coefficient or that the millivoltmeter should be temperature compensated. As an extreme case of this kind, a millivoltmeter having a copper moving coil may have

[2] Electrician (London) **19**, 405 (1887); Elec. World **10**, 160 (1887); British patent no. 3942, issued Dec. 19, 1885.

an internal copper shunt of small current rating (and hence small rise of temperature under load) and the combination will be nearly free from temperature error.

It will be shown later in this paper that in general the use of a current shunt with a compensated millivoltmeter affects the temperature compensation of the combination, used as an ammeter; that this effect is greater, the greater the resistance of the shunt, that is, the smaller the current to be measured; and that a simple procedure may be used to maintain compensation down to values of current so low as to be comparable with the current in the moving coil of the millivoltmeter.

3. EARLIER FORMULAS FOR THE SWINBURNE METHOD OF TEMPERATURE COMPENSATION

Although it was announced in general terms in 1885, the underlying principle of the Swinburne method seems not to have been put into mathematical form until twenty years later. The first such treatment which the author has found is that of Hallo and Land,[3] who derived a simple but incomplete formula which in the symbols of this paper (see fig. 1) is

$$c=b\cdot\frac{\alpha}{\beta-\alpha} \tag{1}$$

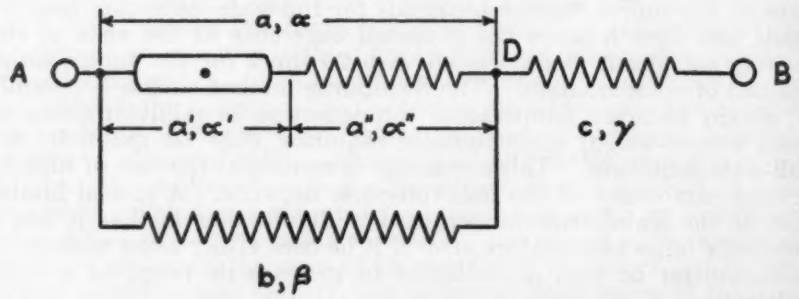

FIGURE 1.—*Diagrammatic plan of circuits of a Swinburne-compensated millivoltmeter.*

The moving coil of resistance a' and temperature coefficient of resistance α' is in series with a manganin coil a''. The temperature coefficient β of coil b is relatively large, γ, that of c, is relatively small, preferably zero. The degree of temperature compensation depends upon the relations between a, b, and c and their temperature coefficients.

In the derivation of this formula Hallo and Land failed to consider the fact that a change in the temperature of the magnet and the springs changes the value of the current in the moving coil for a given deflection.

A more accurate solution, obtained by Heinrich and Bercovitz,[4] was given by them in the form

$$c=b\cdot\frac{\alpha(1+\beta t)}{\beta-\alpha} \tag{2}$$

[3] H. S. Hallo and H. W. Land, Elektrische und Magnetische Messungen und Messinstrumente, p. 259, Berlin (1906). This book is stated to be a free revision and amplification of the Dutch book by G. W. van Swaay, entitled Magnetische en Elektrische Metingen, Delft (1902). A careful search through this latter book revealed no discussion of the Swinburne method of compensation.

[4] Heinke's Handbuch der Elektrotechnik, Bd. 2, Abt. 5, p. 34, (1907).

The symbol α was used by them to denote a pseudo temperature coefficient of resistance, and is defined by them in words of which the following is a translation:

> In this (equation) the temperature coefficient α of the moving coil represents the combined coefficient of the variation of the resistance and of the instrument coefficient of the system.

The term "instrument coefficient" used by these writers is not exactly defined by them but apparently may be taken to denote the temperature coefficient of the deflection with a constant current in the moving coil. This latter coefficient should be brought into the analysis, but not in the manner adopted by Heinrich and Bercovitz. The use of such a composite temperature coefficient in equations dealing with the distribution of current in the branches of a network leads necessarily to an inaccurate result. The formula of Heinrich and Bercovitz, however, contains the term $1+\beta t$, overlooked by Hallo and Land. This term shows that if the millivoltmeter is initially adjusted at some reference temperature it can be exactly compensated for only one other temperature $t°$ different from the reference temperature. Heinrich and Bercovitz did not indicate the manner in which the composite temperature coefficient α was to be experimentally determined.

A few years later, Kollert [5] published the results of what appears to be the first detailed study of the properties and limitations of the Swinburne method. He derived an equation for compensation which agrees in form with that of Heinrich and Bercovitz, eq 2. Like them, he used the symbol α to denote a composite of the temperature coefficient of resistance of the moving-coil branch a (fig. 1) and the temperature coefficient of the deflection with a given current in the moving coil. Kollert indicated the procedure by which the value of this composite temperature coefficient was to be experimentally determined. As in the case of Heinrich and Bercovitz, the use of such a pseudo temperature coefficient could not lead to an exact solution. The true temperature coefficients of resistance of all the branches of a network, and no others, must be used in an analysis to determine the currents in the various branches, and the "instrument coefficient" of Heinrich and Bercovitz, or its equivalent, must be introduced properly as affecting the deflection for a given current but not the distribution of current in the network.

Kollert attacked another phase of the problem, overlooked by previous writers, which may be stated as follows: how should the values of α and b be chosen in order to obtain temperature compensation with a minimum value of e, the full-scale difference of potential at the millivoltmeter terminals, and how large will be this value? His analysis shows that e becomes smaller as b is reduced and reaches a minimum for the impractical case of $b=0$, for which c also must be zero. Too low a value of b gives an undesirably large value of the current required by the millivoltmeter for full-scale deflection. Too large a value of b, on the other hand, requires too large a value of e. Kollert's formula, like its predecessors, has the practical defect of offering a multiply infinite number of solutions, for all of which temperature compensation would be possible (if it were not for the inexactness of the formulas), and from which the instrument designer would have to choose by the cut-and-try method. None of these

[5] Elektrotech Z. **31**, 1219 (1910).

earlier formulas contains anything to guide the designer to the particular solution (or solutions) which provide compensation and also satisfy other requirements to be met.

Campbell,[6] in 1905, described a means for obtaining temperature compensation in direct-current ammeters. He used a Wheatstone bridge in which two diagonally opposite arms had a large temperature coefficient of resistance and the other two had a negligible temperature coefficient. The moving coil of the millivoltmeter mechanism formed one diagonal of the bridge and the ammeter shunt and a pair of connecting leads formed the other diagonal. If the resistance of one of the arms having a high temperature coefficient is made infinite the Campbell network reduces to that of Swinburne. It appears probable that little difference in performance of the two types of network is to be expected. Because of the much greater complexity of the equations for the Campbell network and the somewhat greater complexity in construction which it entails, the author feels that the time which would be required for a complete comparative analysis of the two networks would not be justified.

It is possible to obtain temperature compensation by the use of a magnetic shunt made of a nickel-steel alloy or of one of the more recent copper-nickel-iron alloys, in which the permeability decreases with increasing temperature.[7] This method does not seem to have found commercial acceptance as yet.

IV. EXACT FORMULAS FOR THE SWINBURNE METHOD

1. CURRENT IN THE MOVING COIL AS A FUNCTION OF TEMPERATURE

Referring to figure 2, the straight line *st* represents the constant deflection of a perfectly compensated millivoltmeter as the temperature is varied while the difference of potential between the millivoltmeter terminals is kept constant. The straight line *op* shows the manner in which the current i in the moving coil must vary with the temperature in order to produce this result.[8] Such a variation of current is readily obtained in a millivoltmeter which is compensated by the use of a manganin series resistor only, the proportion of manganin to copper [9] being such as to make the temperature coefficient of resistance dr/dt equal to di/dt, the slope of the line *op*. It will be shown that such a result cannot be obtained by the Swinburne method, with which the current through the moving coil and the deflection for a constant difference of potential between the millivoltmeter termi-

[6] J. Inst. Elec. Engrs. **35**, 197 (1905).

[7] Trans. Am. Inst. Elec. Engrs. **44**, 275 (1925); **49**, 949 (1930).

[8] The slope of *op* is exaggerated for clearness. Actually di/dt may be between 0 and 0.0003. The reason why the current must decrease with increasing temperature, in order to maintain a constant deflection for a constant difference of potential, is to be found in the effects of temperature change upon the magnetic flux density and the strength of the springs. These effects have been discussed in section II, page 490.

[9] Strictly speaking, this should be "the proportion of manganin to the copper equivalent." The alloy springs used in electrical measuring instruments have a temperature coefficient intermediate between those of copper and of manganin. The copper (or aluminum) moving coil and the springs are equivalent, so far as variation of resistance with temperature is concerned, to a copper coil of somewhat greater resistance than the actual coil, in series with a manganin coil having a resistance somewhat less than that of the springs, the sum of these two equivalent resistances being equal, at any temperature, to the sum of the resistances of the coil and the springs. The resistance of this equivalent copper coil may be called, for brevity, the "copper equivalent."

nals will have forms such as $o'p'$ and $s't'$, respectively.[10] With the Swinburne method, therefore, the constants of the network are chosen to make the curve $o'p'$ cut the curve op at points corresponding to chosen temperatures t_1 and t_2, at which the curve $s't'$ will accordingly cut the curve st. The reason for this departure of $o'p'$ from a straight line will appear from the expression for the current i in the moving coil produced by a difference of potential e between the millivoltmeter terminals A and B (fig. 1). This current is

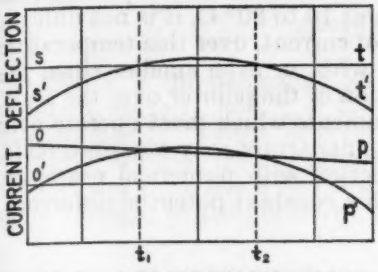

FIGURE 2.—*Curve st represents the constant deflection produced by a current in the moving coil which decreases slightly with increasing temperature as indicated by the sloping line op.*

Curve $s't'$ shows the nonlinear deflection produced by a current in the moving coil which varies with the temperature as represented by the line $o'p'$. A curvature of this general form in the current-temperature curve and in the deflection-temperature curve characterizes the Swinburne method of compensation.

$$i=\frac{b}{a+b}\cdot\frac{e}{c+\frac{ab}{a+b}}$$

$$=\frac{e}{a+c+\frac{ac}{b}}=\frac{e}{q} \qquad (3)$$

The quantity $a+c+ac/b$, denoted for brevity by q, is the resistance of a simple series circuit which is equivalent in every way, so far as the current in the moving coil is concerned, to the actual complex circuit. This equivalent circuit consists of the actual coils a and c and a fictitious coil of resistance ac/b. The presence of this term in the expression for the equivalent series resistance has the same effect in determining the current in the branch a as the actual branch b produces by diverting a part of the total current around the branch a. The equivalent resistance q satisfies the relation

$$q=\frac{e}{i} \qquad (4)$$

If e be kept constant while the temperature is increased the resistance a will increase linearly with the temperature; c will preferably be invariable with temperature, or if necessary, will increase linearly at a very small rate. The term ac/b in the expression for the equivalent resistance is the one which causes the variation of i to be nonlinear. Since c is either invariable or varies linearly, it may be ignored and attention may be given to the manner of variation of its coefficient a/b. The temperature coefficients of a and b being denoted by α and β, the ratio a/b after an increase of t° in the temperature may be written in the form

$$\frac{a(1+\alpha t)}{b(1+\beta t)}=\frac{a}{b}[1-(\beta-\alpha)t+(\beta^2-\alpha\beta)t^2\ .\ .\ .\ .\ .] \qquad (5)$$

[10] The curvature of the lines $o'p'$ and $s't'$, like the slope of the line op, is much exaggerated in the figure.

which shows that when $\beta > \alpha$ (a necessary condition for compensation) the ratio a/b varies in an approximately parabolic manner with temperature. The total current taken by the millivoltmeter does likewise, and because the resistance of each of the branches a and b varies linearly with temperature, it follows that the current in each of these branches varies nonlinearly with temperature. Lest the impression should be given, however, that this curvature in the current-temperature curve is a serious matter, it should be stated that in practice, for moderate ranges of temperature such as 10 to 30° C, it is not difficult to keep the departure from linearity of current, over this temperature range, so small as to be comparable with, or even smaller than, the limit of precision of reading the position of the pointer over the scale. When the method is applied to instruments which must operate over much greater temperature ranges, the departure may be appreciable. Curves will be given later, in connection with numerical examples, showing the change of deflection, with a constant potential difference, over a range of temperature.

2. CASE IN WHICH TEMPERATURE COMPENSATION IS THE ONLY REQUIREMENT

The exact solution of this most general but least useful case of the Swinburne method will now be given, chiefly for comparison with the results of earlier attempts at a solution. It is required to find a relation between the resistances and the temperature coefficients of resistance of the three branches of the Swinburne network (fig. 1) such that the current through the moving coil produced by a constant potential difference between the terminals A and B shall vary with temperature in the manner of $o'p'$, figure 2, and cut the ideal line op at points corresponding to selected temperatures t_1 and t_2.

Referring to eq 3, the current i_1 in the moving coil at temperature t_1 is

$$i_1 = \frac{e}{a_1 + c_1 + \frac{a_1 c_1}{b_1}} \tag{6}$$

This temperature will be regarded as the reference temperature at which the millivoltmeter is adjusted to read correctly. The temperature coefficients [11] α, β, and γ will be based on the reference values of resistance a_1, b_1, and c_1, so that at the higher temperature t_2

$$\begin{aligned} a_2 &= a_1[1+\alpha(t_2-t_1)] \\ b_2 &= b_1[1+\beta(t_2-t_1)] \\ c_2 &= c_1[1+\gamma(t_2-t_1)] \end{aligned} \tag{7}$$

If these values be substituted in eq 6 in place of the values which relate to temperature t_1, the current in the branch a (and hence in the moving coil) at temperature t_2 is

$$i_2 = \frac{e}{a_1[1+\alpha(t_2-t_1)] + c_1[1+\gamma(t_2-t_1)] + \frac{a_1[1+\alpha(t_2-t_1)]c_1[1+\gamma(t_2-t_1)]}{b_1[1+\beta(t_2-t_1)]}} \tag{8}$$

[11] In previous treatments of the subject, to simplify the problem, the branch c has always been assumed to have a temperature coefficient of zero. It will be shown later that γ cannot always be made equal to zero.

This current must be smaller than i_1 to keep the deflection unchanged, and the relation to be satisfied is

$$i_2=\frac{i_1}{1+(t_2-t_1)\delta} \tag{9}$$

The "temperature coefficient of the deflection" δ is defined by the relation

$$\theta_t=\theta_1[1+(t-t_1)\delta], \tag{10}$$

in which θ_1 is the deflection, for a given current in the moving coil, at temperature t_1, and θ_t is the deflection, for the same current, at temperature t. Values of δ for nine instruments examined in this laboratory ranged from $+0.0001$ to $+0.0003$.

It follows from eqs 6 and 9 that for equality of deflections for the same voltage, at temperatures t_1 and t_2, i_2 must satisfy the equation

$$i_2=\frac{e}{\left(a_1+c_1+\frac{a_1c_1}{b_1}\right)[1+(t_2-t_1)\delta]} \tag{11}$$

The denominators of the right-hand members of eq 8 and 11 may now be equated, giving

$$a_1[1+(t_2-t_1)\alpha]+c_1[1+(t_2-t_1)\gamma]+\frac{a_1[1+(t_2-t_1)\alpha]c_1[1+(t_2-t_1)\gamma]}{b_1[1+(t_2-t_1)\beta]}$$

$$=\left(a_1+c_1+\frac{a_1c_1}{b_1}\right)[1+(t_2-t_1)\delta] \tag{12}$$

from which

$$c_1=\frac{b_1(t_2-t_1)(\alpha-\delta)}{1+\frac{a_1+b_1}{a_1}(t_2-t_1)\delta-\frac{b_1}{a_1}(t_2-t_1)\gamma-\frac{[1+(t_2-t_1)\alpha][1+(t_2-t_1)\gamma]}{1+(t_2-t_1)\beta}} \tag{13}$$

The c coil should preferably be made of wire of negligible temperature coefficient, as assumed by previous writers. Putting [12] $\gamma=0$ in eq 13 reduces it to the form

$$c_1=\frac{b_1(\alpha-\delta)}{\frac{a_1+b_1}{a_1}\delta+\frac{\beta-\alpha}{1+(t_2-t_1)\beta}} \tag{14}$$

This exact expression for the resistance of the coil c, in which the temperature coefficient δ of the constant-current deflection has been correctly introduced, is only slightly more involved than the inexact expressions hitherto published. The presence of the quantity t_2-t_1 in eq 13 and 14 shows that exact compensation is theoretically possible for only one temperature other than the one at which the instrument is adjusted. In comparing the exact expression, eq 14,

[12] It is desirable to have $\gamma=0$, and when the millivoltmeter is to indicate the difference of potential between its terminals γ would always be made zero. When the millivoltmeter is calibrated to indicate the potential difference at its terminals plus the drop in a pair of copper leads, it is necessary to use eq 13 because the leads are effectively part of the c coil.

with those given by earlier writers, it should be noted that although the temperature coefficient δ is much smaller than β or α it appears in the equation multiplied by $(a+b)/a$, which in a good design may have a numerical value of 5 or more; and furthermore, this *multiple* of δ is here associated with the *difference* of β and α. The necessity for the use of the exact formula is evident.

3. IMPORTANT REQUIREMENTS OTHER THAN COMPENSATION

The formulas given by previous writers, as well as eqs 13 and 14 just given, are of academic interest but of little value to the instrument designer because they fail to take account of three practical requirements, all of which must be considered in the design of a high-grade compensated millivoltmeter. These requirements are (a) the millivoltmeter must give full-scale deflection for a stated round value of potential difference, for example, 50 or 100 millivolts; (b) its resistance should have a specified round value, for example, 10 ohms; and (c) the motion of the moving coil should be properly damped. Formulas are given in this paper for the conditions to be met for temperature compensation with any one of these three additional requirements; for compensation with any two of them; and for compensation with all three of them. This last case, because of its great usefulness to the instrument designer, will be taken up first and will be treated in much greater detail than the other six cases.

4. COMPENSATION WITH SPECIFIED FULL-SCALE POTENTIAL DIFFERENCE, SPECIFIED RESISTANCE OF THE MILLIVOLTMETER, AND SPECIFIED TOTAL DAMPING RESISTANCE

It is assumed that the designer has a particular millivoltmeter mechanism [13] for which the resistance a_1' of the moving coil and springs (at reference temperature t_1) is known, as well as the current i_{f1} which will produce full-scale deflection at this temperature. The finished millivoltmeter is to give full-scale deflection, at reference temperature t_1 and a second chosen temperature t_2, for a stated potential difference e_f between its terminals; the resistance of the millivoltmeter, at reference temperature t_1, is to be r_1. There is also specified a total damping resistance d_1, which relates to the use of the millivoltmeter with a shunt and is defined (see fig. 3) as the sum of the resistances a_1' and a_1'', plus the resultant resistance of b_1 and c_1 in parallel. It is assumed in this definition that the resistance of the shunt S in figure 3 is negligibly small in comparison with the other resistances involved. Figure 3 is introduced at this point merely to illustrate the significance of the "total damping resistance" thus arbitrarily defined. The following analysis, however, relates to the case of the millivoltmeter used without a shunt, and should be read with reference to the diagram of figure 1.

It is convenient to replace the specified full-scale potential difference e_f and the known full-scale current i_f by a quantity which will

[13] The term "mechanism" as applied to indicating electrical instruments is defined as follows in American Standards for Electrical Indicating Instruments, in preparation at this writing:

"The mechanism of an indicating instrument is the arrangement of parts for producing and controlling the motion of the pointer. It includes all the essential parts necessary to produce these results but does not include the base, cover, scale, or any parts, such as series resistors or shunts, whose function is to adapt the range of the instrument to the quantity to be measured."

be called the "sensitivity resistance" and will be denoted by the symbol s. It is given by the equation

$$s=\frac{e_f}{i_f} \tag{15}$$

and is simply the total resistance which the millivoltmeter would have if its electrical circuit consisted only of the moving coil and springs, plus enough series resistance to make the full-scale deflection correspond to a potential difference e_f between the terminals.[14] This quantity s is really a special value of q which complies with a required value of e_f and the value of i_f which applies to a particular mechanism. It might have been designated by the symbol q with a special subscript, but for simplicity it is designated by the symbol s. The subscript 1 indicates the value which corresponds to reference temperature.

It is required to find (1) the values of a_1, b_1, and c_1 which will give r_1 and d_1 the required values and also satisfy the requirement as to e_f; and (2), to find the values of the temperature coefficients α, β, and γ which will cause the deflection at temperature t_2 to be the same as at

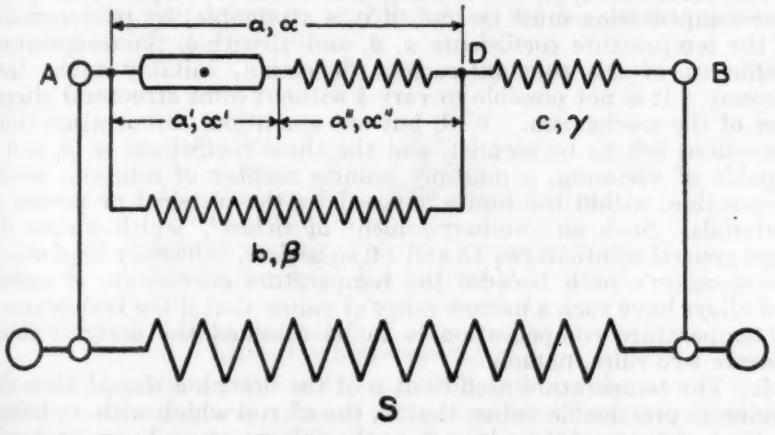

FIGURE 3.—*Diagram of a Swinburne-compensated millivoltmeter connected to a shunt S for the measurement of current.*

the temperature t_1, for the same potential difference between the millivoltmeter terminals. To begin with (1) it is necessary to have three equations which involve a_1, b_1, c_1, r_1, s_1, and d_1.

A comparison of eq 6 and 15 will show that s_1 must be equal to q_1, that is,

$$s_1=a_1+c_1+\frac{a_1c_1}{b_1} \tag{16}$$

from which

$$a_1b_1+a_1c_1+b_1c_1-b_1s_1=0 \tag{17}$$

The resistance of the millivoltmeter at reference temperature is

$$r_1=\frac{a_1b_1}{a_1+b_1}+c_1 \tag{18}$$

from which

$$a_1b_1+a_1c_1+b_1c_1-a_1r_1-b_1r_1=0 \tag{19}$$

[14] Instead of expressing e_f and i_f in volts and amperes, it is convenient to express e_f in millivolts and i_f in milliamperes. Each procedure gives s in ohms.

The total damping resistance at the reference temperature is

$$d_1=a_1+\frac{b_1c_1}{b_1+c_1} \tag{20}$$

from which

$$a_1b_1+a_1c_1+b_1c_1-b_1d_1-c_1d_1=0 \tag{21}$$

Eq 17, 19, and 21 uniquely determine the values of a_1, b_1, and c_1, without any reference whatever to the matter of temperature compensation. The solution of these three equations gives

$$a_1=\frac{s_1d_1(s_1-r_1)}{s_1^2-d_1r_1} \tag{22}$$

$$b_1=\frac{s_1d_1r_1}{s_1^2-d_1r_1} \tag{23}$$

$$c_1=\frac{s_1r_1(s_1-d_1)}{s_1^2-d_1r_1} \tag{24}$$

The values of a_1, b_1, and c_1 being thus fixed, the required temperature compensation must be had (if it is attainable) by proper choice of the temperature coefficients α, β, and γ, with δ, the temperature coefficient of the constant-current deflection, suitably taken into account. It is not possible to vary δ without some structural alteration of the mechanism. With but one condition (temperature compensation) left to be secured, and the three coefficients α, β, and γ capable of variation, a multiply infinite number of solutions would be possible, within the limits imposed by the physical properties of materials. Such an "embarrassment of riches", which makes the most general solutions, eq 13 and 14, so useless, is happily kept out of the designer's path because the temperature coefficients of metals and alloys have such a narrow range of values that if the best degree [15] of temperature compensation is to be attained the designer must observe two rules, namely:

(a) The temperature coefficient α of the branch a should have the minimum practicable value; that is, the a'' coil which with a'_1 brings up the resistance of the a branch to the value a_1 given by eq 22 should be of manganin.[16]

(b) The temperature coefficient γ of the coil c should be zero, if possible. If the use of copper leads, included in the calibration of the millivoltmeter, makes a + value of γ unavoidable, all of the rest of the c branch should be of manganin.

The values of α and γ thus being disposed of, the problem of temperature compensation is reduced to the determination of the value of β. It may be pointed out here that a failure to observe either of rules (a) and (b) gives an undesirable increase in the necessary value of β and increases the departure of the line $o'p'$ from op, figure 2. Upper limits for β, for a reference temperature of 20° C, are about 0.004 for copper and 0.006 for very pure iron and very pure nickel. The difficulties attending the commercial use of iron or nickel make it very desirable to be able to use copper in the b branch, or a suitable

[15] The best degree of temperature compensation is attained, for a given millivoltmeter mechanism and set of requirements, when the current-temperature curve $o'p'$ (fig. 2) departs from the ideal curve op by the minimum possible amount for temperatures between the specified upper and lower limits.

[16] It is theoretically possible to use an alloy for a'' with a slight negative temperature coefficient, but the reduction of α so obtained would be very small. Furthermore, some of the alloys with negative temperature coefficients of resistance are objectionable because their high thermal emf against copper might cause errors.

combination of a copper coil and a manganin coil in series, if the required value of β is lower than the temperature coefficient of pure copper.

An explicit solution for β was derived and used in the course of the present investigation. It was so cumbersome, however, that a more practical procedure was sought and found. It consists of an explicit solution for b_2, from which β may readily be found, and is carried out as follows:

Values of a_1, b_1, and c_1 having been computed by the use of eq 22 to 24, inclusive, α is computed on the assumption that the coil a'' is to be of manganin, and γ is assumed to be zero unless copper leads [17] are to be included in the calibration, in which case the small + value of γ is computed from the resistance of the two leads and that of the (manganin) c coil itself. Values of a_2 and c_2 are then computed by the appropriate formulas, eq 7. Then the equivalent series resistance (compare eq 3) at temperature t_2 is

$$q_2 = a_2 + c_2 + \frac{a_2 c_2}{b_2} \tag{25}$$

To maintain the deflection unchanged at the higher temperature, b_2 must have a value such that

$$q_2 = q_1[1 + (t_2 - t_1)\delta] \tag{26}$$

that is,

$$a_2 + c_2 + \frac{a_2 c_2}{b_2} = \left(a_1 + c_1 + \frac{a_1 c_1}{b_1}\right)\left[1 + (t_2 - t_1)\delta\right] \tag{27}$$

in which the only unknown is b_2. The solution gives

$$b_2 = \frac{a_2 c_2}{\left(a_1 + c_1 + \frac{a_1 c_1}{b_1}\right)\left[1 + (t_2 - t_1)\delta\right] - a_2 - c_2} \tag{28}$$

$$= \frac{a_2 c_2}{s_1[1 + (t_2 - t_1)\delta] - a_2 - c_2} \tag{29}$$

After the numerical value of b_2 has been found by substitution in this equation, the numerical value of β may be found from the relation

$$\beta = \frac{b_2 - b_1}{b_1(t_2 - t_1)} \tag{30}$$

With a reference temperature of 20°C, for example, if the required value of β is 0.0039 or less, the b coil can be made of copper, or partly of copper and the remainder of manganin. If β must be greater than 0.0039 but not over 0.0058, it will be necessary to make the b coil of iron or nickel, alone or in combination with wire having a temperature coefficient lower than that of these metals. Extremely pure iron or nickel is necessary to attain the figure 0.0058 at reference temperature of 20° C. If the value of β as computed from eq 30 exceeds 0.0058, the chosen requirements are too exacting to be realized with materials now available.

The copper, iron, or nickel part of the b branch should be constructed and mounted so that its temperature will follow that of the moving coil very closely. Some tests by the author show that sufficient attention has not always been given to this point. The

[17] One of the copper leads virtually forms part of the coil c (fig. 1) and the other lead, though connected to the terminal A, is electrically also a part of coil c.

method adopted by him consists in winding the copper part of the b branch on a brass spool which is held firmly by a screw to the under side of the brass bracket which supports the scale plate.

5. NUMERICAL EXAMPLE OF THE PRECEDING CASE

Example 1.—A millivoltmeter mechanism of good (though not the most modern) design was available for a practical trial of the formulas developed in the preceding section. The desirable slightly under-damped motion of the coil occurred when the resistance across its terminals was 5.7 ohms. Its essential data were as follows:

Resistance a_1' of moving coil and springs, at $t_1=20°$ C	1.564 ohms.
Temperature coefficient α' of resistance of moving coil and springs, at 20° C	0.0034/° C.
Current i_{f1} in moving coil for full-scale deflection, at 20° C	3.634 ma.
Temperature coefficient δ of the constant-current deflection	0.0001/° C.
Total resistance d_1 for the desired slightly under-damped motion of coil, at 20° C	7.264 ohms.

The second chosen temperature t_2, at which the compensation should be exact, was 30° C. The desired full-scale potential difference e_f was 50 millivolts. The "sensitivity resistance" is (see eq 15)

$$s_1=\frac{e_f}{i_{f1}}=\frac{50}{3.634}=13.759 \text{ ohms.}$$

The resistance r_1 of the millivoltmeter must be less than s_1. The value desired was 10 ohms. The substitution of the values of s_1, r_1, and d_1 in eq 22 to 24, inclusive, gives the following values:

$$a_1=3.220 \text{ ohms.}$$

$$b_1=8.5665 \text{ ohms.}$$

$$c_1=7.660 \text{ ohms.}$$

It was assumed that the millivoltmeter would be adjusted to read the potential difference between its terminals, and hence γ was taken as zero. Consequently, $c_2=c_1=7.660$ ohms. It was also assumed that a'' would be of manganin, of zero temperature coefficient, consequently,

$$\begin{aligned} a_2&=a_1+a_1'\alpha'(t_2-t_1) \\ &=3.220+(1.564\times 0.0034\times 10) \\ &=3.273 \text{ ohms.} \end{aligned}$$

The substitution of this value, with those of c_2, s_1, t_1, t_2, and δ in eq 29, gives

$$b_2=8.8286 \text{ ohms.}$$

The substitution of this value, with those of b_1, t_1, and t_2, in eq 30, gives

$$\beta=0.00306$$

These computed results may be checked as follows:

The resistance of the millivoltmeter at reference temperature, by eq 18, is

$$r_1=7.660+\frac{3.220\times 8.5665}{3.220+8.5665}$$

$$=10.000 \text{ ohms.}$$

The total damping resistance at reference temperature, by eq 20, is

$$d_1=3.220+\frac{8.5665\times 7.660}{8.5665+7.660}$$

$$=7.264 \text{ ohms.}$$

The equivalent series resistance q_1 at reference temperature, by eq 3, is

$$a_1+c_1+\frac{a_1c_1}{b_1}=3.220+7.660+\frac{3.220\times 7.660}{8.5665}$$

$$=13.759 \text{ ohms.}$$

The correctness of the computed value of β may be checked as follows: At the temperature $t_2=30°$ the equivalent series resistance becomes

$$a_2+c_2+\frac{a_2c_2}{b_2}=3.273+7.660+\frac{3.273\times 7.660}{8.8286}$$

$$=13.773 \text{ ohms.}$$

The current which 50 millivolts will pass through this resistance is 50/13.773=3.6303 milliamperes. The current required to produce

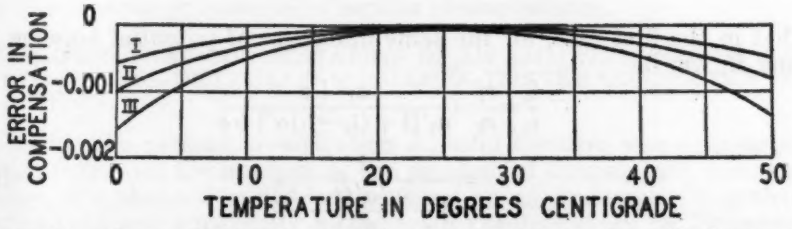

FIGURE 4.—*Curves showing the error in compensation for the millivoltmeter of example 1.*

Curve *I* is for the optimum condition for which α is a minimum and $\gamma=0$. Curve *II* is for $\beta=0.004$ and α increased correspondingly. Curve *III* is for the minimum value of α, $\gamma=0.0002$, and β correspondingly increased.

full-scale deflection at 30° C is 3.634/1.001 equals 3.6304 milliamperes. The small discrepancy in these two results, which corresponds to an imperceptibly small fraction of a scale division, is the result of "rejection error" in the calculations and not of any inexactness of the formulas used.

In figure 4, curve *I* shows the computed performance of the millivoltmeter compensated as in the above example. To illustrate the desirability of keeping α and γ as low as possible, two other curves are shown; *II*, in which β is arbitrarily made equal to 0.004 and α is raised to 0.00208 to correspond; *III*, in which α has its desirable minimum value but γ is given the value 0.0004, which compels β to take the value 0.00459. It may be noted that the curve *I* shows

the least departure from the ideal straight-line compensation. The need for keeping γ low is seen from the fact that giving it the value 0.0004, which is equivalent to making the c coil of one-tenth copper and nine-tenths manganin, raises β to a value which makes some iron (or nickel) necessary in the b coil and triples the departure from compensation as compared with the optimum condition.

V. USE OF A MILLIVOLTMETER WITH A SHUNT FOR MEASURING CURRENT

1. TEMPERATURE COMPENSATION OF A SIMPLE SERIES-COMPENSATED MILLIVOLTMETER

Figure 5 shows diagrammatically the circuit of a simple series-compensated millivoltmeter. Its resistance at temperature t_1 is

$$r_1=a_1'+c$$

and at temperature t_2 is

$$r_2=a_1'[1+\alpha'(t_2-t_1]+c$$

on the assumption that the resistance c is unaffected by the change of temperature. Then the ratio of the current in the second case to

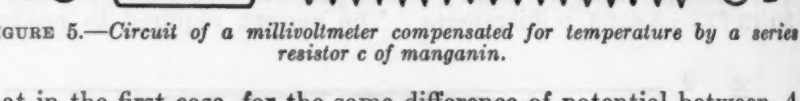

FIGURE 5.—*Circuit of a millivoltmeter compensated for temperature by a series resistor c of manganin.*

that in the first case, for the same difference of potential between A and B, will be

$$\frac{i_2}{i_1}=\frac{r_1}{r_2}=\frac{a_1'+c}{a_1'[1+(t_2-t_1)\alpha']+c}$$

$$=\frac{1}{1+\dfrac{a_1'\alpha'(t_2-t_1)}{a_1'+c}} \tag{31}$$

The decrease in the current at the higher temperature t_2 will not reduce the deflection by the same relative amount because of the greater current sensitivity of the millivoltmeter mechanism at the higher temperature. This effect, already mentioned, is numerically stated in terms of the temperature coefficient δ of the constant-current deflection, and because of it the ratio of the deflection θ_2 at temperature t_2 to the deflection θ_1 at temperature t_1 will be

$$\frac{\theta_2}{\theta_1}=\frac{i_2}{i_1}[1+(t_2-t_1)\delta] \tag{32}$$

Combined with eq. 31, this gives

$$\frac{\theta_2}{\theta_1}=\frac{1+(t_2-t_1)\delta}{1+\dfrac{a_1'\alpha'(t_2-t_1)}{a_1'+c}} \tag{33}$$

For exact temperature compensation θ_2/θ_1 becomes unity, and

$$\frac{a_1'}{a_1'+c}\cdot\alpha'=\delta \tag{34}$$

Thus for the usual average values, $\alpha'=0.004$ and $\delta=0.0002$, c must be 19 times a'_1 for exact compensation. If c is less than $19a_1'$, the millivoltmeter will be under-compensated, and θ_2 will be less than θ_1; if c is greater than $19a_1'$, the millivoltmeter will be over-compensated and θ_2 will be greater than θ_1.

2. USE OF A SHUNT WITH A SIMPLE SERIES-COMPENSATED MILLIVOLTMETER AFFECTS THE TEMPERATURE COMPENSATION

If a millivoltmeter which is wholly or partially compensated for temperature, either by the use of a manganin resistor in series with the moving coil (fig. 5) or by the Swinburne method, be used with a shunt as an ammeter, the degree of compensation as millivoltmeter and as ammeter will (in general) not be the same. The unlikely conditions, for which the degree of compensation will be the same in each case, are that the millivoltmeter and the shunt shall have the same temperature coefficient of resistance and that both shall be at the same temperature when they are used together as an ammeter. Although it is possible to make the shunt of the proportions of manganin and copper which will give the shunt a temperature coefficient of resistance equal to that of the millivoltmeter, it is usually impracticable to keep the shunt and the millivoltmeter at the same temperature. This is particularly true of shunts for large currents, in which the power loss is large enough to raise the temperature of the shunt considerably. It is therefore preferable that the shunt should be of manganin or material of similar characteristics.

3. TEMPERATURE COMPENSATION OF AN AMMETER CONSISTING OF A SERIES-COMPENSATED MILLIVOLTMETER CONNECTED TO A SHUNT

During the present investigation a useful theorem was discovered which facilitates the analysis of the problem of temperature compensation of a shunted millivoltmeter used as an ammeter. Together with an old and apparently little-known theorem given by Feussner, it points out the most convenient and rational values of resistance of shunts to be used with millivoltmeters. For convenience in subsequent reference these two theorems will be numbered.

Theorem 1.—The degree of temperature compensation of a millivoltmeter with a shunt, used as an ammeter, is the same as the degree of temperature compensation which the millivoltmeter would have if it were connected in series with the shunt, now serving as a multiplier, the combination being used as a millivoltmeter. This case is illustrated diagrammatically in figure 6, in which S denotes the shunt and also its resistance, which is assumed for convenience to be invariable with temperature. For this case, by eq 33, the ratio of the deflection at temperature t_2 to the deflection at temperature t_1 is

$$\frac{\theta_2}{\theta_1}=\frac{1+(t_2-t_1)\delta}{1+\dfrac{a_1'\alpha'(t_2-t_1)}{a_1'+c+S}} \tag{35}$$

Now let the connections become those shown in figure 7, which shows the millivoltmeter connected to the shunt in the usual manner for

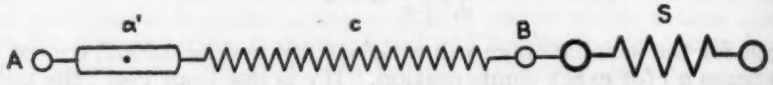

FIGURE 6.—*Series-compensated millivoltmeter connected in series with a shunt S which would normally be in parallel with the millivoltmeter (see fig. 7) for the measurement of a current.*

the measurement of a current I. At the reference temperature t_1 the current through the moving coil of the millivoltmeter will be

$$i_1=\frac{IS}{a_1'+c+S} \tag{36}$$

and the deflection will be θ_1. At temperature t_2,

$$i_2=\frac{IS}{a_1'[1+(t_2-t_1)\alpha']+c+S} \tag{37}$$

$$\frac{\theta_2}{\theta_1}=\frac{i_2}{i_1}[1+(t_2-t_1)\delta] \tag{38}$$

$$=\frac{a_1'+c+S}{a_1'[1+(t_2-t_1)\alpha']+c+S}[1+(t_2-t_1)\delta] \tag{39}$$

$$=\frac{1+(t_2-t_1)\delta}{1+\frac{a_1'\alpha'(t_2-t_1)}{a_1'+c+S}} \tag{40}$$

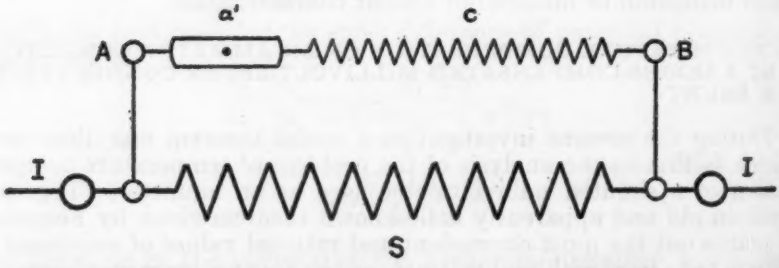

FIGURE 7.—*Series-compensated millivoltmeter connected to a shunt S for the measurement of a current.*

This equation is identical with eq 35. It shows that the resistance S enters the denominator virtually as an increase in the value of c. If c is inadequate for exact compensation as a millivoltmeter, and S is not too large, the compensation as an ammeter will be better than as a millivoltmeter. It may now be seen why the use of manganin shunts for very small currents, the resistance of such shunts being relatively large, introduces relatively large temperature errors by over-compensation, if the millivoltmeter alone is well compensated as such.

An obvious and important consequence of theorem 1 is that if any portion of the series resistor c is removed and put in parallel with the remainder of the millivoltmeter circuit, the portion of c removed being used as a shunt, the degree of temperature compensation as an ammeter will be the same as that of the millivoltmeter in its original condition, used to measure the potential difference at its terminals. This holds true even if *all* of c is used as a shunt, for which case the apparently anomalous condition exists that an all-copper [18] millivoltmeter mechanism, subject to a temperature error of nearly 0.4 percent per degree centigrade when used as a millivoltmeter, will have a zero temperature error when used as an ammeter, with a manganin shunt having a particular value of resistance. This fact shows how a millivoltmeter may be used to measure small currents without the usual large temperature error, namely, by reducing the series resistance c of the millivoltmeter by an amount equal to the resistance of the shunt, if the millivoltmeter as such is entirely compensated. If it is not, and it is desired to make the combination, millivoltmeter and shunt, exactly compensated as an ammeter, the sum of the resistance S of the shunt and the resistance c of the manganin coil in the millivoltmeter should have the value which c ought to have for exact compensation of the millivoltmeter used as such.

The removal of a part of c to serve as a shunt can be effected by the equivalent procedure shown in figure 8. Here the millivoltmeter is

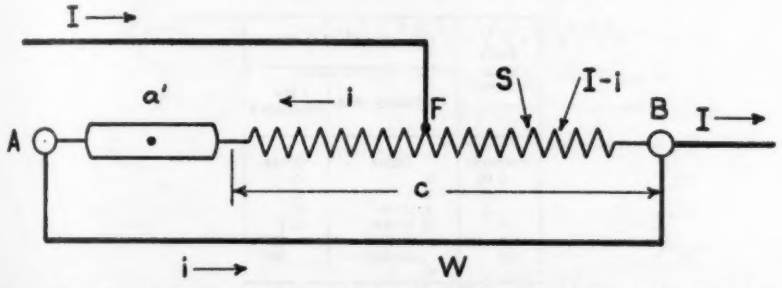

FIGURE 8.—*Series-compensated millivoltmeter with its terminals joined by a wire W of negligible resistance.*

A portion S of the manganin resistor c is used as an ammeter shunt in the measurement of a current I. The degree of temperature compensation is the same as that of the millivoltmeter used alone as such.

shown as short-circuited by a wire W of negligible resistance, and the current I to be measured is introduced at a point F on the resistor c and leaves at the point B.

The ordinary method of using shunts for the measurement of relatively small currents has another disadvantage besides that of affecting the temperature compensation, namely, the resistance of the shunt must be given an odd value which depends upon the resistance of the millivoltmeter. For example, the 1-ohm millivoltmeters used at one time were provided with shunts having resistances of 1/9, 1/99, ------ ohm. A usual resistance for compensated millivoltmeters today is 10 ohms. If the range in millivolts of such instruments is assumed to be the same as for the 1-ohm millivoltmeter, shunts for the former would need to be 10/99, 10/999, ------ ohm.

[18] Strictly, the spiral springs are of alloy with a temperature coefficient less than that of copper, but the statement would nevertheless hold, even if the springs were of copper.

It is desirable not only to avoid the necessity for odd values but also to have the resistance of a shunt, for a given current and a given potential difference, independent of the resistance of the millivoltmeter with which it is to be used. It was shown by Feussner[19] that the use of a part of the series resistance c as the resistance S of a shunt avoids the odd values and makes the resistance of the shunt independent of that of the millivoltmeter. Feussner's principle may be stated as follows:

Theorem 2.—If a millivoltmeter which gives a stated deflection for a potential difference e at its terminals is used with a shunt to measure a current I for which it is to give the same stated deflection, and if the series resistance of the millivoltmeter is reduced by an amount equal to the resistance of the shunt, then the resistance of the shunt will be e/I, regardless of the resistance of the millivoltmeter.

In other words, the resistance of the shunt in this case will have the value it would have if the shunt were to be used with a potentiometer, which is equivalent to a millivoltmeter of infinite resistance. The following table illustrates the difference between the resistances of five shunts which are adjusted in one case for use in the ordinary way with a 10-ohm millivoltmeter which gives full-scale deflection for 100 millivolts, and in the second case for use with this or any other millivoltmeter on the assumption that its series resistance is to be decreased by an amount equal to the resistance of the shunt.

TABLE 1.—*Comparison of resistances of shunts*

Full-scale current	Resistance of shunt	
	Ordinary case	By theorem 2
Amperes	*Ohms*	*Ohms*
0.02	10	5
.05	2.5	2
.1	1.111+	1
1	0.1010+	0.1
10	.01001+	.01
100	.0010001+	.001

Above 10 amperes the differences become of little or no practical significance, but for small currents the advantage of adjustment to the round values of theorem *2* is obvious, especially when it is considered that the odd values of column *2* would be different for millivoltmeters of different resistances.

It follows from theorem *2* that if the series resistor c be tapped to form a multirange shunt, as shown in figure 9, the resistances of the various sections CB of the shunt will be inversely as the corresponding currents for a stated deflection of the millivoltmeter. Thus, theorem *2* includes the principle of the Ayrton-Mather universal galvanometer shunt. The theory of this shunt, however, as given by its inventors and by others since them, does not include the fact of which theorem *2* is a statement.

[19] Elektrotech. Z. 25, 115 (1904).

It is obvious that if part of the series resistor c is to be used as an ammeter shunt its cross section and its opportunity for giving off heat must be suitably increased. What is thought to be the most suitable method of utilizing the two theorems is shown in figure 10.

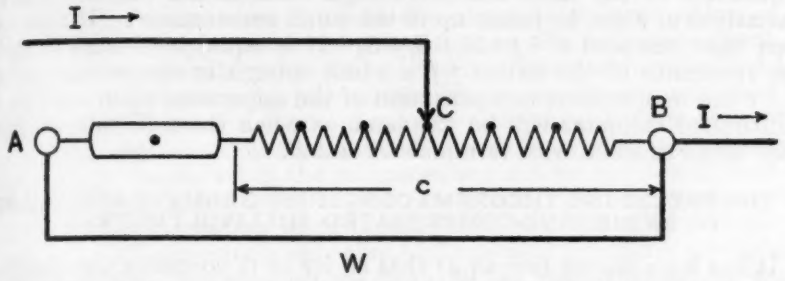

FIGURE 9.—*Series-compensated millivoltmeter with its terminals joined by a wire W of negligible resistance.*

The series resistor c has a number of tap points traversed by the brush C. The apparatus constitutes a multirange ammeter. Each range has the degree of temperature compensation which the millivoltmeter has when used alone as such.

Here three manganin resistors, S_1, S_2, and S_3 are permanently connected in series to form an Ayrton-Mather set of three ammeter shunts of resistances S_1, S_1+S_2, and $S_1+S_2+S_3$ respectively. A' and

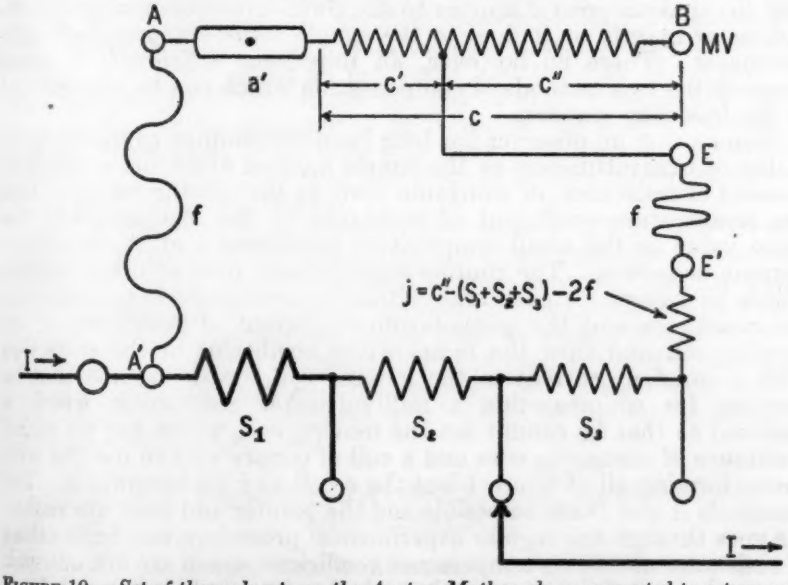

FIGURE 10.—*Set of three shunts on the Ayrton-Mather plan, connected to a temperature-compensated millivoltmeter through a tap point on the series resistor c.*

When the coil f has the value indicated the temperature compensation of each current range is the same as that of the millivoltmeter used alone as such.

E' are the potential terminals of the shunt, and are removably attached to the millivoltmeter terminals A and E by links or flexible cords $f\,f$ of resistance which is either negligible or is allowed for in

the adjustment of the coil marked j. It should be noted that the tap wire to the terminal E is brought out from a point which divides the resistance c into parts c' and c'', c'' being say three-fourths of c. This makes it possible to standardize the value of c'' for all millivoltmeters of the same nominal design because the manufacturing variations of c can be taken up in the small resistance c'. It may be seen that the sum $c'+j+S_1+S_2+S_3+2f$ is equal to c, and that if the resistance of the cables $f\,f$ is small enough in comparison with $a'+c$ the temperature compensation of the apparatus when used as a multirange ammeter will be the same as when the millivoltmeter is used alone as such, with terminals A and B.

4. THE PRECEDING THEOREMS CONCERNING SHUNTS APPLY ALSO TO SWINBURNE-COMPENSATED MILLIVOLTMETERS

It has been shown (see eq 3) that so far as it concerns the magnitude of the current i in the moving coil a' when a potential difference e is applied to the terminals A and B (see fig. 1), the network may be replaced by an equivalent simple series circuit consisting of the moving coil a and the coil c plus an increment ac/b to the coil c. It may readily be shown, in the manner used in the preceding section, (a) that the degree of temperature compensation of a Swinburne-compensated millivoltmeter, used with a shunt as an ammeter, is the same as the degree of compensation which would exist if the shunt were put in series with the millivoltmeter to extend its range as such; and (b) that theorem *2* applies to the Swinburne-compensated millivoltmeter exactly as it does to the simple series-compensated millivoltmeter. There is, however, an important difference of detail between the two methods of compensation which can be brought out in the following manner:

Assume that an observer has long been accustomed to the compensation of millivoltmeters by the simple method of adding a sufficient amount of resistance, of manganin wire, to the moving coil to reduce the temperature coefficient of resistance of the instrument to the same value as the small temperature coefficient δ of the constant-current deflection. The routine experimental part of the procedure which he follows for each millivoltmeter mechanism is to determine the resistance and the temperature coefficient of resistance of the moving coil and then the temperature coefficient of the deflection with a constant current in the moving coil. Now assume that he receives for compensation a millivoltmeter mechanism which is enclosed so that he cannot see the moving coil, which has an added resistance of manganin wire and a coil of copper wire in parallel with them, forming all of figure 1 but the c coil and its terminal B. The terminals A and D are accessible and the pointer and scale are visible. He goes through the regular experimental procedure and finds values of resistance and of its temperature coefficient which are not unusual. On passing a definite current through the supposed simple coil, however, at the two temperatures, he is surprised to find that the constant-current deflection increases by as much as 0.2 percent per degree centigrade; in other words, that δ has an abnormal value about 10 times as great as would usually be found. He may lay this fact to the use of some new alloy for the springs, which seem to weaken, with a given increase of temperature, much more than all alloy springs he has previously tested; or to the use of an unusual kind of magnet

steel for which the flux density in the air gap seems to increase with temperature at a rate previously unknown. In any event, the high value of δ shows him that this particular mechanism may be compensated by the use of a manganin coil c (fig. 1) having the relatively low resistance which will make the temperature coefficient of resistance of the instrument equal to the abnormally large value of δ. It will then be apparent to him that the use of a manganin shunt, of resistance comparable with that of the millivoltmeter, will affect the compensation by say 0.1 percent per degree centigrade; and that in the extreme case of a shunt of infinite resistance (that is, when the millivoltmeter is used as a milliammeter with the whole current passing through it) the defect in the compensation will be equal to δ, that is, it may be 0.2 percent per degree centigrade. For comparison, the defect in compensation when a series-compensated millivoltmeter is used as a milliammeter is only about 0.02 percent per degree centigrade.

The above reasoning shows that in the measurement of small currents with Swinburne-compensated millivoltmeters and relatively high-resistance manganin shunts much greater defects in temperature compensation exist than when series-compensated millivoltmeters are used. This fact has long been known. Keinath [20] states that the current in the shunt must be at least 10 times the instrument current, and that for the Siemens 10-ohm millivoltmeter, for example, the range of the smallest regularly listed shunt is 150 milliamperes, that is, over 30 times the instrument current. He adds that shunts are supplied for lower values down to 15 milliamperes but that these are applicable only for less accurate measurements. He states that the temperature error in this latter case may be compensated by making the shunt partly of manganin and the rest of copper, but that this procedure introduces the risk of error because the copper may be heated by the current in it and in the adjacent manganin and the instrument as a whole may show a temperature error. For this reason he concludes that this method of constructing shunts for small currents is inadvisable.

In contrast with this unsatisfactory state of affairs, the arrangement shown in figure 10 permits the use of a Swinburne-compensated millivoltmeter for currents as small as (for example) twice the instrument current with a degree of temperature compensation at least as good as that of the millivoltmeter used as such. If the millivoltmeter is only partially compensated when used alone, it is possible to choose the values of shunts, of even very low ranges, such that the compensation may be complete when the millivoltmeter is used with the shunts as an ammeter.

VI. MULTIRANGE SWINBURNE-COMPENSATED INSTRUMENTS

1. MULTIRANGE MILLIVOLTMETERS

Figure 11 shows the manner in which a second, higher range would be provided in a simple series-compensated millivoltmeter. An additional manganin coil c' is provided and also a coil of copper wire Cu in close thermal proximity to the moving coil. If the temperature compensation of the first range (for the case of terminals A and

[20] Die Technik elektrischer Messgeräte, 1st ed., p. 60; 2d ed., p. 66; 3d ed., vol. 1, p. 106.

B) is exact, and that of the second range is also to be exact, the temperature coefficient of resistance of the part *BB'* would be made equal to that of the part *AB*; that is, equal to the value of δ for the particular millivoltmeter mechanism. Because of the relatively

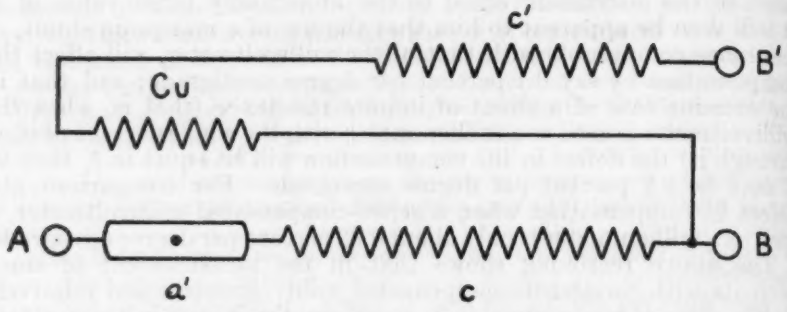

FIGURE 11.—*Method of adding a second millivolt range to a series-compensated millivoltmeter, with maintained temperature compensation.*

The copper coil *Cu* and the second manganin coil *c'* must have jointly the same temperature coefficient of resistance as the moving coil *a'* and the original manganin coil *c*.

small resistance of the coil *Cu* as compared with that of *c'* the necessary degree of equality of temperature of *Cu* and *a'* is very moderate for this case of simple series compensation.

Figure 12 shows the same procedure as applied to a Swinburne-compensated millivoltmeter. The principle of this case is exactly

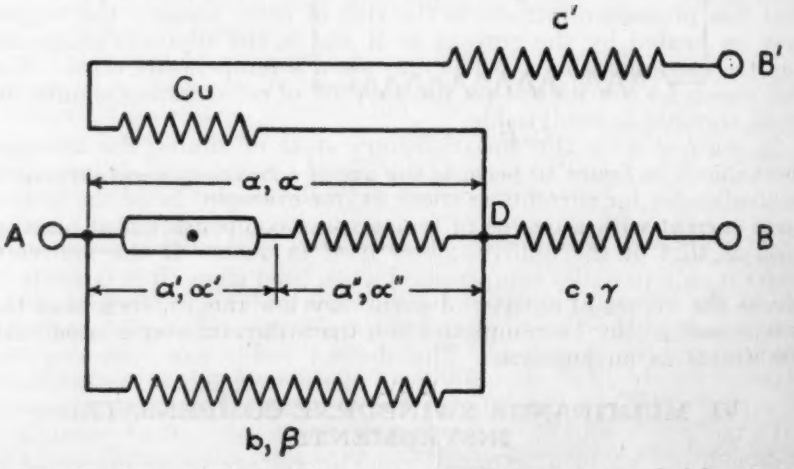

FIGURE 12.—*One method of adding a second millivolt range to a Swinburne-compensated millivoltmeter.*

To maintain the original degree of temperature compensation the temperature coefficient of resistance of the network with *A* and *B'* used as terminals must be the same as when *A* and *B* are used as terminals. The same value of ohms per volt applies to both ranges.

the same as that of the preceding case, in that the temperature coefficient of resistance of the part *D Cu B'* is made equal to that of the part *ADB*. In the Swinburne case, however, the relative amount of resistance in the coil *Cu* is so much greater that this coil

should be so made and supported as to follow the temperature of coils a' and b very closely. This method of obtaining higher ranges is simple and gives the same number of ohms per volt on all ranges, but its use is preferably limited to higher ranges which are in the millivolt class. For still higher ranges another method is preferable.

2. COMBINED VOLTMETER-MILLIVOLTMETERS ("VOLT-MILLIVOLTMETERS")

When a Swinburne-compensated millivoltmeter is to be provided with a higher range (or ranges) which in turn are to be capable of indefinite extension by the use of external multipliers, the method described in the preceding section is not at all suitable. If used, it would require that for every one of the higher ranges a corresponding value of resistance of the coil *Cu* in figure 12 would have to be provided. It would not answer the purpose to put these sections of the copper

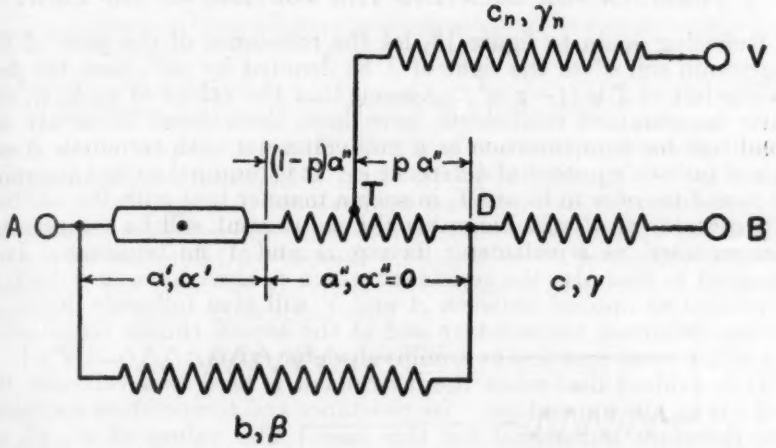

FIGURE 13.—*The Schöne method of adding a temperature-compensated volt range to a Swinburne-compensated millivoltmeter.*

A tap is brought out from a particular point T on the manganin resistor a'', and a manganin resistor c_n joins T to the terminal V for the volt range. This method gives a volt range having a random value of ohms per volt.

coil in the external multiplier because unavoidable differences in the temperature of these sections and of the moving coil would impair the temperature compensation. The desired result can, however, be obtained simply and accurately by a method originated by Schöne.[21] It is shown diagrammatically in figure 13, and consists in bringing out a tap from a suitable point T on the manganin coil a'', through a manganin coil c_n, to a terminal V. The voltage to be measured is applied between the terminals A and V, and the coil c of the network is idle. If the temperature coefficient δ of the constant-current deflection were equal to zero, and if the resistance of c_n were very high in comparison with that of the moving coil a', the tap point on a'' would be chosen so that the temperature coefficient of a' plus the part of a'' to the left of the tap point T would be equal to the temperature coefficient of b plus the part of a'' to the right of T. In the usual case

[21] O. Schöne, letter to editor, Elektrotech. Z. 33, 201 (1912).

of a small positive value of δ and for a relatively high value of c_n, the tap point must be to the left of this position so that for a constant voltage between A and V (and hence a nearly constant current in c_n, regardless of temperature changes) the current in the moving coil will decrease with temperature at a rate equal to δ. For a particular, relatively low value of c_n and with a small positive value of δ the point T would be chosen to give equal temperature coefficients to the two paths to the right and to the left of T. In this case the decrease in the current through the moving coil, at the higher temperature, results from the decrease in the current taken by the millivoltmeter because of the presence of copper in a' and b. For still lower ranges the point T must move to the right in order to give the moving coil a greater share, at the higher temperature, of the decreased current taken by the voltmeter as a whole. For still lower ranges T shifts further to the right until in the limit it coincides with D for $c_n=c$.

3. FORMULA FOR LOCATING THE VOLTMETER TAP POINT

Referring again to figure 13, let the resistance of the part of the manganin coil a'' to the right of T be denoted by pa'', then the part to the left of T is $(1-p)a''$. Assume that the values of a_1, b_1, c_1, and their temperature coefficients have been determined to satisfy the condition for compensation as a millivoltmeter with terminals A and B and full-scale potential difference e. It is required to find the value of p, and thereby to locate T, in such a manner that with the addition of a resistor c_n of suitable value the instrument will be temperature compensated as a voltmeter having A and V as terminals. It is required to find also the resistance which c_n must have in order that a voltage ne applied between A and V will give full-scale deflection at the reference temperature and at the second chosen temperature for which compensation as a millivoltmeter exists.

It is evident that when the instrument is used as a voltmeter the coil c is an idle appendage. Its resistance and temperature coefficient are therefore immaterial for this case. The values of a', a'', α', b, and β must be left unchanged. It is assumed that α'' is zero, since it is disadvantageous to have it otherwise. The temperature compensation as a voltmeter will depend upon the location of the tap point T, and upon the magnitude and the temperature coefficient γ_n of the coil c_n. It is usually desirable to have γ_n negligibly small by making the coil c_n of manganin. There are thus two unknowns, p and c_n, and two independent equations connecting them are required. The first one is obtained by ignoring the original coil c and considering the remainder of the network as a Swinburne-compensated network in which the original branch a $(=a'+a'')$ has become $a'+(1-p)a''$, the original b coil has become $b+pa''$, and the new coil c_n replaces the original coil c. These new branches must satisfy an equation for temperature compensation, of the form of eq 14, namely,

$$c_{n1}=(b_1+pa'')\frac{\alpha_n-\delta}{\frac{a_1+b_1}{a_1+(1-p)a''}.\delta+\frac{\beta_n-\alpha_n}{1+(t_2-t_1)\beta_n}} \tag{41}$$

in which the temperature coefficients of the new a and b branches are

$$\alpha_n = \frac{a'_1\alpha'}{a'_1+(1-p)a''} \tag{42}$$

$$\beta_n = \frac{b_1\beta}{b_1+pa''} \tag{43}$$

The values of resistance of the three new branches must also satisfy the condition that the new equivalent series resistance q_n must be n times the original q as a millivoltmeter; that is, for the reference temperature t_1

$$a'_1+(1-p)a''+c_{n1}+\frac{[a'_1+(1-p)a'']c_{n1}}{b_1+pa''}=n\left(a_1+c_1+\frac{a_1c_1}{b_1}\right) \tag{44}$$

The condition that p shall satisfy eq 41 and 44 leads to the quadratic equation

$$p^2+\frac{\{(ns_1-a_1)(a_1\alpha+b_1\beta)-(ns_1\delta-a_1\alpha)(a_1+b_1)-a_1b_1(\beta-\alpha)\}p}{a''(a_1\alpha+b_1\beta)}-$$
$$-\frac{b_1\{(ns_1\delta-a_1\alpha)(a_1+b_1)[1+(t_2-t_1)\beta]+(ns_1-a_1)a_1(\beta-\alpha)\}}{a''^2(a_1\alpha+b_1\beta)}=0 \tag{45}$$

The solution of this equation for p, if left in its conventional form, would evidently be very inconvenient for use in computing numerical values, especially for the case of multirange voltmeters for which p must be computed for several values of n. The following exact formula is the result of an effort to express p in such a way as to minimize the labor of computation:

$$p=nP\frac{-\left(1-\frac{S}{n}\right)+\left[\left(1-\frac{S}{n}\right)^2+\frac{4(n-1)U}{n^2}\right]^{\frac{1}{2}}}{2} \tag{46}$$

in which

$$P=\frac{s_1[a_1(\alpha-\delta)+b_1(\beta-\delta)]}{a''(a_1\alpha+b_1\beta)} \tag{47}$$

$$S=\frac{2a_1b_1(\beta-\alpha)}{s_1[a_1(\alpha-\delta)+b_1(\beta-\delta)]} \tag{48}$$

$$U=\frac{b_1\{(a_1+b_1)[1+(t_2-t_1)\beta]\delta+a_1(\beta-\alpha)\}(a_1\alpha+b_1\beta)}{s_1[a_1(\alpha-\delta)+b_1(\beta-\delta)]^2} \tag{49}$$

It should be noted that the denominator of S is the same quantity as the numerator of P, and the denominator of U is that quantity squared and multiplied by s_1. In the expression for p, eq 46, the quantities S/n and $4(n-1)U/n^2$ are small in comparison with unity, and the square root of the quantity in brackets, after numerical substitution, may be obtained conveniently by using only a few terms of the expansion

$$(1\pm\epsilon)^{\frac{1}{2}}=1\pm\frac{\epsilon}{2}-\frac{\epsilon^2}{8}\pm\frac{\epsilon^3}{16}\cdots\cdots \tag{50}$$

It should be noted, however, that the square root of the quantity in brackets in eq 46 is only slightly larger numerically than the negative

quantity $-(1-S/n)$ to which it is to be added, and consequently these quantities must be correct to such a number of significant figures as will ensure that their small difference shall be sufficiently accurate. This small difference is multiplied by the large quantity nP to obtain the value of p.

The use of even the simplified formulas, 46 to 50, is so laborious as to justify some special comments. If the added range is greater than the original range by only a small factor, say 2 to 5, these formulas are required, as in the case of a millivoltmeter with a basic range of 50 millivolts and an added range of 100 millivolts. Aside from such cases, however, the added range will usually be a relatively large multiple of the basic range; for example, 1.5 volts with a basic range of 50 millivolts. In this case $n=30$ and the values of p for this and all higher ranges will not differ greatly from each other or from the value for $n=\infty$. For this last case the exact formula, eq 50a, in the following paragraph is very much less laborious, and it should ordinarily be used to determine a single tap point to serve for the 1.5-volt and all higher ranges.

Two limiting values of p are of interest. If $n=1$, $p=0$, as is evident from inspection of eq 46. This condition is simply that of the original range as a millivoltmeter, and signifies (see fig. 13) that the tap point T coincides with the point D. The other limiting case is that of $n=\infty$, for which

$$\underset{n=\infty}{p}=PU$$

$$=\frac{b_1\{(a_1+b_1)[1+(t_2-t_1)\beta]\delta+a_1(\beta-\alpha)\}}{a''[a_1(\alpha-\delta)+b_1(\beta-\delta)]} \tag{50a}$$

This is the value of p which locates the tap point T (fig. 13) from which a wire would be brought out to a binding post to provide a temperature-compensated milliampere range. Since the value of p for $n=\infty$ is a limiting value which is asymptotically and closely approached by the usual volt ranges, and since this value of p is the easiest one to compute, it should be computed first. If it is less than 1, or even if it exceeds 1 by a small amount, it will be possible to provide volt ranges in the intended manner. If p for $n=\infty$ materially exceeds 1, only relatively low compensated volt ranges can be added.

It must not be inferred that in actual practice a separate tap point T would be used for each volt range. This would complicate the construction and unduly increase the cost of the instrument. Instead, after computing p for the desired ranges, the designer would choose a value intermediate between the extreme values, thus providing theoretically exact compensation only for some intermediate range. The ranges above this one would be slightly over-compensated, that is, the indication for a constant voltage would increase slightly with increasing temperature. Ranges below the chosen intermediate range would be slightly under-compensated. In an actual case, however, these defects of compensation may be so small as to be either impossible to detect or if just discernible they may be negligible in the practical use of the instrument. This matter may best be illustrated by a numerical example based on the millivoltmeter mechanism which formed the starting point for example *1* (see p. 512).

4. NUMERICAL EXAMPLES OF METHOD OF LOCATING THE VOLTMETER TAP POINT

Example 2.—The values of a_1', α', i_{f1}, δ, r_1, s_1, t_1, and t_2 were as given in example 1, but the value of total damping resistance d_1 was reduced to 6.56 ohms. This was done because it was planned to bring out a voltmeter tap, and the reduction in d_1 would improve the damping when the instrument was used as a voltmeter. The use of eq 22 to 24 gave the following values:

$$a_1=2.7426 \text{ ohms.}$$
$$b_1=7.2960 \text{ ohms.}$$
$$c_1=8.0067 \text{ ohms.}$$

Consequently:

$$a''=a_1-1.564$$
$$=1.1786 \text{ ohms.}$$
$$\alpha=(1.564\times 0.0034)/2.7426$$
$$=0.00194/°\text{C.}$$
$$a_2=2.7426+(1.564\times 0.0034\times 10)$$
$$=2.7958 \text{ ohms.}$$

The value of γ is taken as zero, hence $c_2=c_1=8.0067$ ohms. Using eq 29, the value of b_2 is found to be 7.5364 ohms. Hence, by eq 30,

$$\beta=\frac{7.5364-7.2960}{7.2960\times 10}=0.00329$$

The values of p computed by eq 46 to 50 from the preceding data are as follows:

$n=$	30	100	300	1,000	3,000	10,000	30,000	∞
Volts	1.5	5	15	50	150	500	1,500	∞
$p=$	1.0031	1.0260	1.0326	1.0349	1.0355	1.0358−	1.0358	1.0358+

These values of p are carried to more decimal places than would be used in practice, in order to show the very small change in p for this large range of values of n.

In practice, it is impossible to have values of p greater than unity. The value $p=1$ signifies that the tap point T coincides with the junction of the coils a' and a''. Before dismissing the above example as impractical, however, it should be assumed that the value $p=1$ will be used for all ranges, and the extent of the departure from compensation should be computed. Before this can be done, it is necessary to find the value of r_n, the resistance of the higher range, and of c_n (see fig. 13).

The resistance of the higher range at reference temperature is

$$r_{n1}=\frac{ne_f}{i_{n1}}=\frac{ne_f}{\frac{i_1(a_1+b_1)}{(pa''+b_1)}}=\frac{ne_f(pa''+b_1)}{i_1(a_1+b_1)} \tag{51}$$

The resistance of the part of the higher range which is composed of $a_1'+(1-p)a''$ in parallel with $pa''+b_1$ is

$$r_{n1}-c_{n1}=\frac{[a_1'+(1-p)a''](pa''+b_1)}{a_1+b_1} \tag{52}$$

and consequently

$$c_{n1}=\frac{ne_f(pa''+b_1)}{i_1(a_1+b_1)}-\frac{[a_1'+(1-p)a''](pa''+b_1)}{a_1+b_1} \tag{53}$$

After the value of r_{n1} has been computed for one range, with a given value of p, values of r_{n1} for the higher ranges will be in proportion to their full-scale voltages. Also, the second term on the right in eq 53 need be computed only once, as far as values at reference temperature are concerned. Its value should be computed for the higher temperature t_2 also. It is convenient to assume that the c coils are to be of manganin of negligibly small temperature coefficient.

The use of these formulas in the case of example 2 with p taken as equal to 1 for all ranges, gives the following results:

At reference temperature, 20° C, the calculated values are

$$r_{n1}-c_{n1}=1.3203 \text{ ohms.}$$
$$r_{n1}, \text{ for } n=30, =348.46 \text{ ohms.}$$
$$c_{n1}, \text{ for } n=30, =347.14 \text{ ohms.}$$

The values of r_{n1} for higher values of n will be in direct proportion to n, for example,

$n=$	30	100	300	1,000	3,000
$ne_f=$	1.5	5	15	50	150 volts
$r_{n1}=$	348.46	1,161.5	3,484.6	11,615	34,846 ohms

At the higher temperature $t_2=30°$ C, $r_{n2}-c_{n2}$ will be 1.3640 ohms, that is, it will be 0.0437 ohm greater than $r_{n1}-c_{n1}$. On the assumption that the values of c_n are invariable with temperature, each of the values of r_{n2} will be 0.0437 ohm greater than the corresponding r_{n1}. The values of the current i_n in the branch c_n produced by full-scale voltage ne_f will thus be slightly less at 30° than at 20°. The defect in the compensation for any range may be computed in a way which will be illustrated by applying it to the extreme ranges, namely, the 1.5- and 150-volt ranges. In order to demonstrate the exactness of the formulas and the high degree of compensation which can theoretically be obtained by their use, many of the values in this and in subsequent numerical examples are carried to a greater number of significant figures than would be warranted by the possible precision of reading the indication of the instrument.

For the 1.5-volt range,

$$i_{n2} \text{ at } 30° \text{ C}=1.5/348.5037=0.004,304,1 \text{ ampere}$$

Of this current, the part i_2 in the moving coil is

$$\frac{(a''+b_2)i_{n2}}{a_2+b_2}=\frac{8.7150\times 0.004,304,1}{2.7958+7.5364}$$
$$=0.003,630,42 \text{ ampere}$$

At 30° C the current in the moving coil to produce full-scale deflection, with δ taken into account, is $0.003,634/1.001=0.003,630,37$ ampere. The discrepancy is thus 0.000,000,05 ampere, which is 1 part in 70,000, which is equivalent to about 0.002 division in a deflection of 150 divisions. An error in compensation ten times as great as this could hardly be detected by the most careful observer. It is

thus entirely permissible to use the round value $p=1$ for the 1.5-volt range.

For the 150-volt range,

$$i_{n2} \text{ at } 30°=150/34,846=0.004,304,7 \text{ ampere}$$

Of this current the part through the moving coil is

$$\frac{8.7150\times 0.004,304,7}{10.3322}=0.003,630,9 \text{ ampere}$$

The current should be 0.003,630,4 ampere. The actual current will be too large by 0.000,000,5 ampere, that is, it is too large by 1 part in 7,200, which is equivalent to about 0.02 division in a deflection of 150 divisions. This discrepancy in the current is in the direction opposite to the discrepancy for the 1.5-volt range, and is negligibly small. Similar calculations show that the round value $p=1$ can be used for all ranges above 1.5 volts without discernible error.

If the computed values of p had exceeded 1 by an amount so large that the use of $p=1$ would have resulted in objectionable defects in the temperature compensation of the higher ranges, it would have been necessary to revise the requirements to bring p down to a practical value. It is not possible to increase s without making some structural change in the mechanism, and it is usually desirable to hold r at a standard value. This leaves d as the most eligible quantity to be revised, because the requirements as to damping are not rigid. To exhibit the effect on p of a change in d, the next example will differ from example 2 only in that d is increased.

Example 3.—Let $s_1=13.759$ ohms, $r_1=10$ ohms, $d_1=7$ ohms. These values, substituted in eq 22 to 24, give the following values:

$$a_1=3.0345 \text{ ohms.}$$
$$b_1=8.0725 \text{ ohms.}$$
$$c_1=7.7946 \text{ ohms.}$$

Also,

$$\alpha=(1.564\times 0.0034)/3.0345=0.00175$$
$$a''=3.0345-1.564=1.4705 \text{ ohms.}$$
$$a_2=3.0345+(1.564\times 0.034)$$
$$=3.0877 \text{ ohms.}$$

With $t_2-t_1=10°$, $\delta=0.0001$, and $c_2=c_1=7.7946$ ohms, the use of eq 29 gives

$$b_2=8.3259 \text{ ohms.}$$

The use of this value in eq 30 gives

$$\beta=0.00314.$$

Values of p computed by eq 46 to 50 are as follows:

$n=30$ (1.5-volt range) $p=0.9652$.
$n=\infty$ $p=0.9965$.

Comparison of these values of p with those of example 2 shows that if d_1 were given the value 6.78 ohms (the mean of the values of d_1 in examples 2 and 3) the values of n for the above two limiting cases would probably be about $1-0.016$ and $1+0.016$, respectively. This may be considered as the ideal case, for the defect in the compensation, with one compromise value of p $(=1)$ for all ranges, will have negligibly small values for the extreme values of n and still smaller values for intermediate values of n. It is easily shown, however, that even for $d=7$ and the resulting values of p the defect in compensation will be negligible for the 1.5-volt and all higher ranges. The computed values of defect in compensation are 0.015 percent for $n=30$ and 0.002 percent for $n=\infty$.

5. METHOD FOR OBTAINING A ROUND VALUE OF OHMS PER VOLT IN THE VOLT RANGES

Instead of stating the current required by a voltmeter for full-scale deflection, American makers usually express the sensitivity of the voltmeter by stating the reciprocal of this current, which is given as so many "ohms per volt." Its value is found by dividing the resistance of any range of the voltmeter by the full-scale voltage for this range.

It has been shown in the preceding section that if a Swinburne-compensated millivoltmeter be provided with a tap on the a'' coil for a higher range, the value of ohms per volt for this higher range will be greater than for the original millivolt range. Furthermore, even in millivoltmeters which are nominally identical and are adjusted to identical values of resistance and of millivolts for full-scale deflection, the values of ohms per volt, for a given higher range, will not be identical because of variations in spring strength and magnet strength of individual instruments. It is good practice to have a round and standardized value of ohms per volt for the millivolt range, and it is even more desirable for the volt range (or ranges) because such standardization permits the use of interchangeable multipliers with standardized round values of resistance in their various sections. If the millivoltmeter has a round value of ohms per volt, it will usually be advisable to adopt the same value of ohms per volt for the added volt ranges. An excessive reduction of the ohms per volt of the volt ranges is not advisable if it can be avoided.

A method for bringing the added higher range down to a desired value of ohms per volt has been used for many years by a prominent German manufacturer, but no description of the method has been published, so far as the author of this paper is aware. It will be described with reference to figure 14, which shows the network of figure 13, plus an added branch of resistance m. This new branch is in parallel with a current path composed of the moving coil a', the part $(1-p)a''$ of the manganin coil a'', and the part v of the series resistor c_n for the higher range. A part of the current taken by the voltmeter is diverted around the moving coil by the coil m. The effect is similar to that which would result from a reduction in the sensitivity because of a weakening of the magnet or an increase in the strength of the springs. If the coil c_n had the correct value before the application of the coil m, it will be necessary, after applying m, to cut out of circuit a part of c_n as is done (fig. 14) by bringing out a tap from the point T'' on c_n to the binding post V', in order that the

specified voltage shall produce full-scale deflection. The small portion of c_n to the right of T''' and the terminal V are then to be discarded. The problem is to find suitable values of m, v, and w which will give the desired round value of ohms per volt for the range having the terminals A and V'. There is no unique solution. The desired value of ohms per volt may be obtained by the use of any one of an infinite number of values of m with corresponding values of v and w. Because an arbitrary choice of m must be made, and also because the analysis would probably become very involved, it has not seemed desirable to develop a general expression for the network of figure 14 with which to determine by a single solution the values of all the branches in such a way as to provide the basic range as a millivoltmeter and the higher range, of a definite number of ohms per volt, with temperature compensation for each range. Instead, it seems much better first to

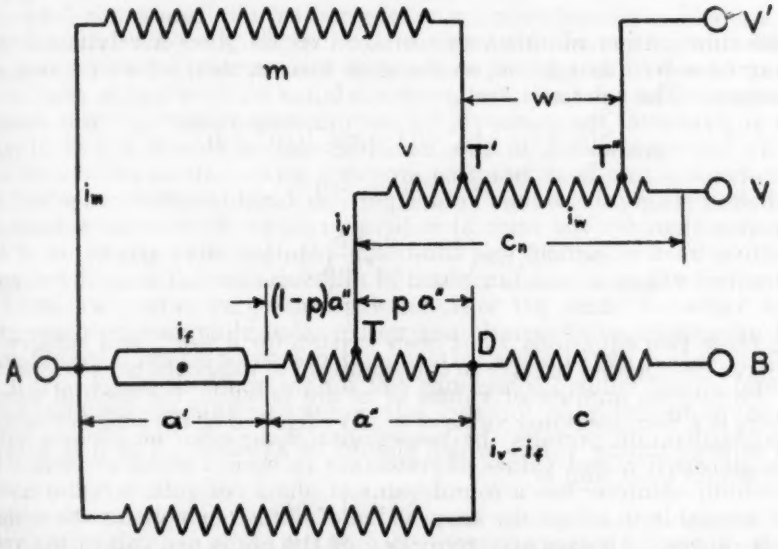

FIGURE 14.—*Swinburne-compensated millivoltmeter in which an added volt range originally consisting of a coil c_n joining the tap point T to a terminal V has been given a desired round value of ohms per volt by the addition of the coil m and the terminal V' connected to the tap point T''.*

determine the values of a, b, c, and β to satisfy the requirements for the millivolt range; then to compute values of p for the higher ranges and to choose a suitable compromise value of p which minimizes the defects of compensation of the higher ranges; then to compute c_n for the lowest volt range, as if no shunt coil m would be used. These steps having been taken, it becomes necessary to take account of the coil m.

Referring to figure 14, let it be assumed that the volt range having the terminals A and V' has the desired value y of ohms per volt, the reciprocal of which value is the current i_w in the branch w for full-scale deflection. This current divides at the point T' into a current i_m through m and a current i_v through v. The current i_v divides at T into two parts, one of which is the current i_f in the moving coil for full-scale deflection.

The current in v is

$$i_v=\frac{(a'+a''+b)i_f}{pa''+b} \tag{54}$$

The potential difference between the points A and T' is

$$\begin{aligned} mi_m&=vi_v+[a'+(1-p)a'']i_f \\ &=\frac{v(a'+a''+b)i_f}{pa''+b}+[a'+(1-p)a'']i_f \end{aligned} \tag{55}$$

Also,

$$i_m=i_w-i_v \tag{56}$$

$$=i_w-\frac{(a'+a''+b)i_f}{pa''+b} \tag{57}$$

The substitution of this value of i_m in eq 55 gives a relation which may be solved first for m, as if v were known, then for v as if m were known. The solutions are

$$m=\frac{v(a_1+b_1)+[a_1'+(1-p)a''](pa''+b_1)}{\frac{i_{w1}}{i_{f1}}(pa''+b_1)-(a_1+b_1)} \tag{58}$$

$$v=\frac{(pa''+b_1)\left\{m\left(\frac{i_{w1}}{i_{f1}}-\frac{a_1+b_1}{pa''+b_1}\right)-[a_1'+(1-p)a'']\right\}}{a_1+b_1} \tag{59}$$

In these two equations a has been written for $a'+a''$, and subscripts 1 have been added to refer to the condition of reference temperature t_1.

An infinite number of values of m are possible, for each of which there is a corresponding value of v. At each end of the series of values of m are limiting values which should be avoided. The first is that for which $v=0$, and is

$$\underset{v=0}{m}=\frac{a_1'+(1-p)a''}{\frac{i_w}{i_f}-\frac{a_1+b_1}{pa''+b_1}} \tag{60}$$

This value of m will be relatively low. The addition of this coil to the network will cause the maximum disturbance in the performance of the instrument as a millivoltmeter, and will consequently require a greater revision of the original values of a, b, c, and β. A further probable disadvantage is that this low value of m may cause overdamping. There is no compensating advantage in using it and it may be dismissed from further consideration.

The other limiting value of m is that for which the coil m is connected between the points A and V. The current taken by m has then little effect on the performance of the instrument, other than to make it take more current than it would if m were absent. In other words, the coil m is merely a little additional load on the source whose voltage is being measured. This case has the advantage of producing the minimum disturbance of the damping and of the performance of the instrument as a millivoltmeter but it has an objectionable feature which should exclude it from use. If the coil m, connected

between the points A and V, should become open-circuited, the performance as a voltmeter with these points as terminals would be unaffected and the defect would not be revealed by a check of this range. All higher ranges, however, would be in error. This limiting value of m is given by the formula

$$m_{s=c_n} = \frac{r_n y n e_f}{r_n - y n e_f} \tag{61}$$

in which r_n is the resistance of the volt range with terminals A and V, the coil m not having been applied; ne_f is the full-scale value of voltage for this range, and y is the desired number of ohms per volt.

In the choice of an intermediate value of m the following suggestions may be useful. First, m should have several hundred times the resistance of the moving coil a' plus the part $(1-p)$ of the coil a'', in order that the addition of m may produce only a very small effect on the performance of the instrument as a millivoltmeter. The value of m should not be so high, however, as to make w small in comparison with v. If the voltage range which has A and V' as terminals is of only a few volts, a satisfactory value of m may be one which makes v and w approximately equal. If this range, however, is of say 10 or 15 volts, the value of m for $v=w$ may be needlessly high, and it would be better to take a round value of m of, say 1,000 ohms, and let v be relatively small in comparison with w. In the search for a suitable value of m eq 58 may be used with trial values assumed for v, beginning with $v=c_n/2$. The values of m having been plotted as a function of v, inspection of the curve will facilitate the choice of a round value of m (in general, a multiple of 100 ohms) for which v is not much greater than $c_n/2$. Then the chosen value of m may be substituted in eq 59 to obtain the exact value of v.

The next step is to determine the value of w. Referring to figure 14, the resistance between the points A and V' may be put equal to the full-scale voltage, ne, either divided by the current i_w which the voltmeter range is to require for full-scale deflection, or (what is the same thing) multiplied by y, the required number of ohms per volt. The resistance w will be equal to this total resistance, yne, minus the resultant resistance of the network between the points T' and A; that is, for the condition of reference temperature t_1,

$$w = yne - \frac{m\left\{v + \dfrac{[a_1' + (1-p)a''](pa'' + b_1)}{a_1' + a'' + b_1}\right\}}{m + v + \dfrac{[a_1' + (1-p)a''](pa'' + b_1)}{a_1' + a'' + b_1}}$$

$$= yne - \frac{m\{v(a_1 + b_1) + [a_1' + (1-p)a''](pa'' + b_1)\}}{(m+v)(a_1 + b_1) + [a_1' + (1-p)a''](pa'' + b_1)}$$

The next step is to take care of the fact that the indications of the instrument, used as a millivoltmeter, will now be too low because of the diversion of part of the current away from the moving coil. In general, it would be necessary to revise the values of a_1, b_1, c, and β to take account of this added current patb. Then a revised value of p would have to be computed, as well as revised values of v and w for the chosen m, which could remain unchanged. Theoretically,

these changes would cause a slight change in the accuracy of the millivoltmeter, and the values of a_1, b_1, c, and β would need another (though much smaller) readjustment, which would in turn call for revision of the values of p, v, and w, and so on. Such a process of repeated readjustment would be laborious, but a special expedient has been found which makes it unnecessary.

It may be seen from figure 14 that any change in the resistance of the coil c will have no effect on the added volt range, and also that any necessary readjustments of pa'' and of b_1 will have no effect on the volt range if the sum of these two resistances is kept unchanged. These latter readjustments are equivalent to sliding the junction point D along $pa''+b_1$, and with a suitable change in c they provide the means for readjusting the accuracy of the millivolt range without any reaction on the accuracy of the volt range at reference temperature. In determining the original values of a_1, b_1, and c_1 for the millivolt range, eq 22 to 24 were used. These equations express three conditions to be satisfied, namely, prescribed values of sensitivity resistance s_1, millivoltmeter resistance r_1, and total damping resistance d_1. One of these requirements must now give way to make room for the condition that pa'' and b_1 are to change as may be necessary while their sum is to remain constant. The sensitivity of the mechanism, which determines s_1, is not to be changed, and it is desirable that r_1 should retain its original value. This leaves d_1 as the quantity which can best undergo any small change which will result from the revision of the initial values of a_1, b_1, and c_1.

Referring to figure 14, let the network consisting of $a'+(1-p)a''$ shunted by $v+m$ be regarded as an equivalent moving coil with terminals at A and T. Its resistance at temperature t_1 is

$$a'_{eq1}=\frac{[a_1'+(1-p)a''](m+v)}{a_1'+(1-p)a''+m+v} \tag{63}$$

On the preferable assumption that a'', m, and v have zero temperature coefficient of resistance, the resistance of the equivalent moving coil at temperature t_2 is

$$a'_{eq2}=\frac{[a_2'+(1-p)a''](m+v)}{a_2'+(1-p)a''+m+v} \tag{64}$$

The temperature coefficient of resistance of the equivalent moving coil, assumed as linear over the temperature range t_1 to t_2, is

$$\alpha'_{eq}=\frac{a'_{eq2}-a'_{eq1}}{a'_{eq1}(t_2-t_1)} \tag{65}$$

The current in the equivalent moving coil for full-scale deflection θ_1 at temperature t_1 is

$$(i_f)_{eq1}=\frac{[a_1'+(1-p)a''+m+v]i_{f1}}{m+v} \tag{66}$$

where i_{f1} is the current in the actual moving coil. From eq 66, for full-scale deflection θ_1,

$$i_{f1}=\frac{m+v}{a_1'+(1-p)a''+m+v}\cdot(i_f)_{eq1} \tag{67}$$

If the current in the equivalent moving coil be kept at the value $i_{f)eq1}$ and the temperature be raised to t_2, a'_1 in eq 66 will become a'_2 and the current in the actual moving coil will decrease accordingly. Its value becomes

$$i_2=\frac{m+v}{a_2'+(1-p)a''+m+v}\cdot(i_f)_{eq1} \tag{68}$$

This reduction in i tends to make the deflection θ_2, at temperature t_2, lower than θ_1. This tendency, however, is opposed by the action of the temperature increase on the magnet and springs, of which δ is the measure. The ratio of the deflection at the higher temperature t_2 to the deflection at reference temperature t_1 will be

$$\frac{\theta_2}{\theta_1}=\frac{a_1'+(1-p)a''+m+v}{a_2'+(1-p)a''+m+v}\cdot[1+(t_2-t_1)\delta] \tag{69}$$

and the temperature coefficient of the deflection, for the equivalent moving coil, is

$$\delta_{eq}=\frac{\frac{\theta_2}{\theta_1}-1}{t_2-t_1} \tag{70}$$

The "sensitivity resistance" of the equivalent moving coil at reference temperature t_1 is, by eq 15 and 16,

$$s_{eq1}=\frac{e_f}{(i_f)_{eq1}}=\frac{e_f(m+v)}{[a_1'+(1-p)a''+m+v]i_{f1}} \tag{71}$$

The resistance a'_{eq1}, temperature coefficient of resistance α'_{eq}, temperature coefficient of deflection δ_{eq}, and sensitivity resistance s_{eq1} having been determined by eq 63, 65, 70, and 71, the problem is now to determine, on the basis of the equivalent moving coil, revised values a_r, b_r, and c_r to satisfy two of the previous requirements for the millivolt range, namely, a prescribed full-scale potential difference e_f and a prescribed resistance r of the millivoltmeter. These two requirements are expressed in forms identical with those of eq 17 and 19, and are

$$a_{r1}b_{r1}+a_{r1}c_{r1}+b_{r1}c_{r1}-b_{r1}s_{eq1}=0 \tag{72}$$

$$a_{r1}b_{r1}+a_{r1}c_{r1}+b_{r1}c_{r1}-a_{r1}r_1-b_{r1}r_1=0 \tag{73}$$

in which the additional subscripts 1 denote the values at reference temperature t_1.

The third equation, which expresses the new requirement that the sum of pa'' and b is to remain constant, and which displaces equation 21 concerning the damping, may be written

$$a_{r1}+b_{r1}-a'_{eq1}-b_1-pa''=0 \tag{74}$$

The solution of these three equations gives the following results:

$$a_{r1}=\frac{(a'_{eq1}+pa''+b_1)(s_{eq1}-r_1)}{s_{eq1}} \tag{75}$$

$$b_{r1}=\frac{(a'_{eq1}+pa''+b_1)r_1}{s_{eq1}} \tag{76}$$

$$c_{r1}=r_1\left[1-\frac{(a'_{eq1}+pa''+b_1)(s_{eq1}-r_1)}{s^2_{eq1}}\right] \tag{77}$$

Values of these three branches at reference temperature t_1, computed by these formulas, will make the indication of the millivoltmeter and its resistance correct at reference temperature. In order that it may be compensated for temperature, a revised value β_r of β is required.

In the revised millivoltmeter network the coil c_r is to be of manganin and the portion pa'' of the original network is to be replaced by a manganin coil having a resistance

$$a_r''=a_{r1}-a'_{eq1} \tag{78}$$

The resistance at temperature t_2 of the new branch a_r will be

$$a_{r2}=a'_{eq2}+a_r'' \tag{79}$$

In order that the deflection as a millivoltmeter shall be the same at temperatures t_2 and t_1 it is necessary (see eq 29) that

$$b_{r2}=\frac{a_{r2}c_{r2}}{s_{eq1}[1+(t_2-t_1)\delta_r]-a_{r2}-c_{r2}} \tag{80}$$

Then

$$\beta_r=\frac{b_{r2}-b_{r1}}{b_{r1}(t_2-t_1)} \tag{81}$$

If m has been chosen sufficiently large with respect to $a'+(1-p)a''$ the increment of resistance per degree, $b_{r1}\beta_r$, will differ only slightly from the original value $b_1\beta$, and the temperature compensation of the voltmeter range (or ranges) will be only slightly changed. If the change is larger than is desired, a slight change may be made in β in order to divide the error of compensation between the volt ranges and the millivolt range.

The method above outlined for bringing the sensitivity of the added volt range down to a round value of ohms per volt was applied to the voltmeter-millivoltmeter developed in example 2, as outlined in the following example.

6. NUMERICAL EXAMPLE OF THE METHOD FOR OBTAINING A ROUND VALUE OF OHMS PER VOLT

Example 4.—This is the case of example 2 (p. 527) with p taken equal to 1 for all ranges from 1.5 volts up, and with the additional requirement that the sensitivity of all of these volt ranges should be

200 ohms per volt. The network[22] for example *2*, with numerical values of resistance indicated, is shown in figure 15. The additional coil m to be supplied, and subdivisions v and w of the coil c_n are indicated. It is the object of this problem to determine values of m, v, w, and the revised values of a_1, b_1, c, and β to give the volt ranges a sensitivity of 200 ohms per volt. The coil c_n and the terminal marked "1.5 volts, 232 ohms per volt" apply to the case of example *2* for which m may be regarded as infinite, for which case $v+w=c_n$.

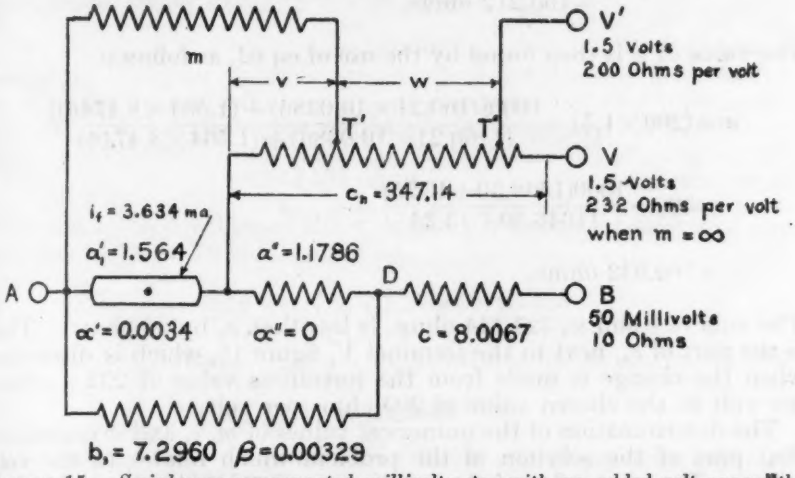

FIGURE 15.—*Swinburne-compensated millivoltmeter with an added volt range, the sensitivity of which is to be brought down from its original random value of 232 ohms per volt to the round value 200 ohms per volt, by the addition of the coil m.*

The numerical values shown apply to the case of the random value of ohms per volt. After the application of m, the values of a'', b_1, and c become 1.1702, 7.3044, and 8.0116 ohms, respectively.

The limiting values of m, which are to be avoided, are by eq 60 and 61

$$m_{v=0} = \frac{1.564+0}{\frac{0.005}{0.003634} - \frac{2.7426+7.2960}{8.4746}}$$

$$= \frac{1.564}{0.1913} = 8.176 \text{ ohms.}$$

$$m_{v=c_n} = \frac{300 \times 348.46}{348.46-300} = 2{,}157 \text{ ohms.}$$

The value of m for $v=c_n/2$, by eq. 58, is

$$m_{v=c_n/2} = \frac{(173.57 \times 10.0386)+(1.564 \times 8.4746)}{\frac{0.005 \times 8.4746}{0.003634} - 10.0386}$$

$$= \frac{1755.65}{1.6217} = 1{,}082.6 \text{ ohms.}$$

[22] It is slightly unfortunate, for the purposes of this example, that $p=1$. The method of computing the revised values of resistance of the coils a, b, and c, however, when p is not equal to 1 can be readily understood. The fact that $p=1$ simplifies the construction by avoiding the necessity for one coil.

Since this odd value of m is associated with an odd value of v, it will be convenient to give m the desirable even value, 1,000 ohms. The corresponding value of v, by eq 59, is

$$v_{m=1,000} = \frac{8.4746\left\{1000\left(\frac{0.005}{0.003634}-\frac{10.0386}{8.4746}\right)-1.564\right\}}{10.0386}$$

$$=160.212 \text{ ohms.}$$

The value of w is then found by the use of eq 62, as follows:

$$w=(200\times1.5)-\frac{1000[(160.21\times10.0386)+(1.564\times8.4746)]}{(1160.21\times10.0386)+(1.564\times8.4746)}$$

$$=300-\frac{1000(1608.30+13.25)}{11646.90+13.25}$$

$$=160.932 \text{ ohms.}$$

The sum of v and w, 321.144 ohms, is less than c_n by 26 ohms. This is the part of c_n, next to the terminal V, figure 15, which is discarded when the change is made from the fortuitous value of 232+ ohms per volt to the chosen value of 200 ohms per volt.

The determination of the numerical values of m, v, and w completes that part of the solution of the problem which relates to the volt range. The remainder of the solution consists of the determination of revised values a_r, b_r, and c_r which will restore the accuracy and the temperature compensation of the millivolt range.

By eq 63, the resistance of the equivalent moving coil at temperature t_1 is

$$a'_{eq1}=\frac{1.564\times1160.212}{1.564+1160.212}=1.5619 \text{ ohms.}$$

At temperature t_2,

$$a'_{eq2}=\frac{1.617176\times1160.212}{1161.829}=1.6149 \text{ ohms.}$$

Consequently, by eq 65,

$$\alpha'_{eq}=\frac{1.6149-1.5619}{1.5619\times10}=0.00339/°\text{C.}$$

By eq 66,

$$(i_f)_{eq1}=\frac{(1.564+1160.212)\times0.003634}{1160.212}$$

$$=0.0036389 \text{ ampere.}$$

By eq 69, the ratio of the deflection θ_2 at temperature t_2 to the deflection θ_1 at temperature t_1, the current in the equivalent moving coil being the same in the two cases, is

$$\frac{\theta_2}{\theta_1}=\frac{1.564+1160.21}{1.617176+1160.21}\times 1.001$$
$$=1.000954$$

from which, by eq 70,

$$\delta_{eq}=0.000095$$

By eq 71,

$$s_{eq1}=\frac{0.050\times 1160.212}{(1.564+1160.212)\times 0.003634}$$
$$=13.7404 \text{ ohms.}$$

Then the revised values of the a, b, and c branches at reference temperature t_1, by eq 75 to 77, must be

$$a_{r1}=\frac{(1.5619+1.1786+7.2960)\times 3.7404}{13.7404}$$
$$=2.7321 \text{ ohms.}$$
$$b_{r1}=\frac{(1.5619+1.1786+7.2960)\times 10}{13.7404}$$
$$=7.3044 \text{ ohms.}$$
$$c_{r1}=10\left[1-\frac{(1.5619+1.1786+7.2960)\times 3.7404}{(13.7404)^2}\right]$$
$$=10(1-0.19884)$$
$$=8.0116 \text{ ohms.}$$

In the revision of the millivoltmeter network the portion pa'' of the original network, having a resistance of 1.1786 ohms, is to have a resistance

$$a''_r=a_{r1}-a'_{eq1}=2.7321-1.5619$$
$$=1.1702 \text{ ohms.}$$

This coil is to be of manganin. The sum of the resistances a''_r and b_r, 1.1702 + 7.3044, equals the sum of the corresponding values before revision, namely, 1.1786 + 7.2960.

The resistance at temperature t_2 (=30° C) of the revised branch a_r will be

$$a_{r2}=a'_{eq2}+a''_r=1.6149+1.1702$$
$$=2.7851 \text{ ohms.}$$

In order that the deflection as a millivoltmeter for a given potential difference shall be the same at $t_1=20°$ and at $t_2=30°$, the resistance of the revised branch b_r at temperature t_2, by eq 80, must be

$$b_{r2}=\frac{2.7851\times 8.0116}{(13.7404\times 1.00095)-2.7851-8.0116}$$

$$=7.5465 \text{ ohms.}$$

The revised value of the temperature coefficient of this coil is, by eq 81,

$$\beta_r=\frac{7.5465-7.3044}{10\times 7.3044}=0.00331/° \text{ C}$$

The correctness of the revised values of a_1, b_1, c, and β may now be checked. The resistance of the millivolt range at 20° C will be

$$r_{20}=8.0116+\frac{2.7321\times 7.3044}{2.7321+7.3044}$$

$$=10.0000 \text{ ohms.}$$

The current taken by this range, with an applied potential difference of 50 millivolts, is 0.005 ampere. Of this, the part through the equivalent moving coil is $(7.3044\times 0.005)/(2.7321+7.3044)$ equals 0.0036389 ampere. Of this, the current in the actual moving coil is $(1160.212\times 0.0036389)/(1.564+1160.212)$ equals 0.003634 ampere.

At 30° C the resistance of the millivolt range will be

$$r_{30}=8.0116+\frac{2.7851\times 7.5465}{2.7851+7.5465}$$

$$=10.0459 \text{ ohms.}$$

The current which 50 millivolts will pass through this range is 0.050/10.0459 equals 0.004,977,15 ampere. Of this, the equivalent moving coil gets $(7.5465\times 0.00497715)/(7.5465+2.7851)$ equals 0.00363545 ampere. Of this, the part through the actual moving coil is $(1160.21\times 0.00363545)/(1160.21+1.617)$ equals 0.0036304 ampere. The current in the moving coil for full-scale deflection is 0.003634/1.001 equals 0.0036304— ampere. The negligible difference between this value and the preceding one is caused by rejection error in the calculations.

By a similar calculation for an intermediate temperature of 25° C it may be shown that for 50 millivolts applied to the millivolt range the current in the actual moving coil will have the correct value for full-scale deflection at that temperature, within 0.003 percent, that is, within 0.005 division in a deflection of 150 divisions. This defect in the compensation is negligible. For temperatures between 20° and 25°, and between 25° and 30°, the defect in the compensation will be smaller than 0.003 percent.

The total damping resistance at reference temperature with the millivoltmeter terminals connected by a wire of negligible resistance is

$$d_{r1}=2.7321+\frac{7.3044\times 8.0116}{7.3044+8.0116}$$

$$=6.5529 \text{ ohms.}$$

The necessary shift in this quantity, resulting from the revision of the branches of the millivoltmeter network, is so small that its effect on the damping would not be discernible.

The remaining matter to be checked is that of the compensation of the volt ranges. The values of p, on the basis of which the approxi-

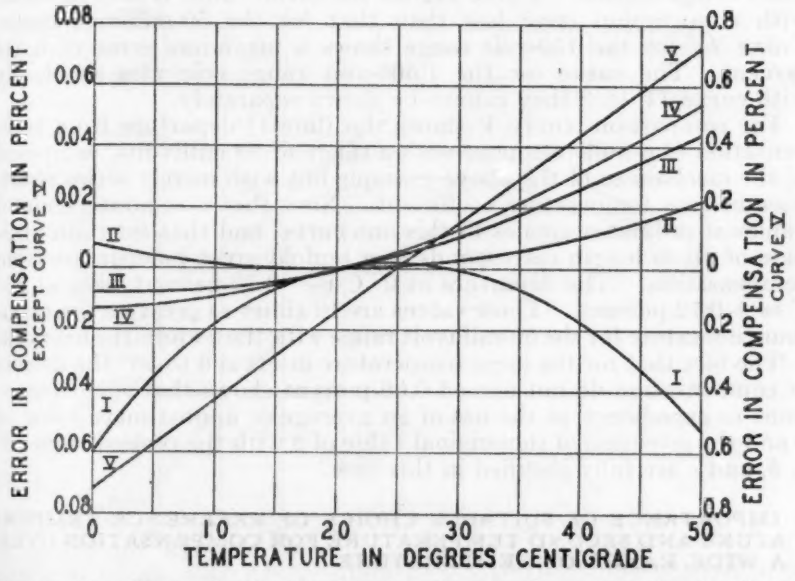

FIGURE 16.—*Curves showing the departure from exact compensation for the volt-millivoltmeter of example 4 when used over a much wider range of temperature than that for which the compensation was designed.*

Curves *I*, *II*, and *III* are for the 50-millivolt, 1.5-volt, and 5-volt ranges, respectively. Curve *IV* applies identically to the 150- and 1,500-volt ranges. Curve *V*, for which a separate scale of ordinates is at the right, shows that the same mechanism, compensated merely with series resistance for the 50-millivolt range, would have departures from compensation more than 10 times as great as those for the Swinburne arrangement.

mate value $p=1$ was selected, were based on $\beta=0.00329$, and the computed revised value $\beta_r=0.00331$. This minute change in β could not affect the compensation appreciably. In fact, it could not be experimentally checked by resistance measurements on the copper coil except under extremely refined conditions because it corresponds to a change of temperature of only 0.005° C in such a coil.

The departures from exact compensation, for the present example, are given in figure 16 for a number of the ranges. To bring out certain characteristics of the Swinburne compensation the values were computed for temperatures from 0 to 50° C, that is, for a range extending 20° below t_1 and 20° above t_2. The typical curve (*I*) for the 50-millivolt range crosses the line of zero departure (line of exact compensation) at 20° and at 30° C, rises to a slight positive value

which is greatest (but entirely inappreciable) near 25°, and falls below the line of exact compensation in approximately parabolic fashion as the temperature decreases from 20° or increases from 30°. It is evident that if the instrument were to be used over the range 0 to 50° the maximum error could be approximately halved by lifting the curve by about one-half of the error at 0°. This could be done readily, without altering any resistance adjustments, if the instrument has an adjustable magnetic shunt. In the given example the magnetic field would need to be increased about 0.03 percent, and the resulting maximum departure from compensation would have this value, negative for 0° and plus for 25°.

Curve *II* for the 1.5-volt range shows the smallest departure from exact compensation. Curve *III* for the 5-volt range is next in order, with a maximum error less than that for the 50-millivolt range. Curve *IV* for the 150-volt range shows a maximum error of 0.054 percent. The curve for the 1,500-volt range coincides so closely with curve *IV* that they cannot be shown separately.

For comparison, curve *V* shows the (linear) departure from compensation of a millivoltmeter with a range of 50 millivolts, composed of the mechanism of the above example but with merely series resistance of zero temperature coefficient. Note that a separate scale of values of ordinates applies to this one curve, and that for it an ordinate of given length corresponds to a tenfold greater departure from compensation. The departure at 0° C is —0.72 percent, that at 50° C is + 0.72 percent. These values are 12 times as great as the maximum departure for the 50-millivolt range with the Swinburne network.

The fact that for the large temperature interval 0 to 50° the defects of compensation do not exceed 0.06 percent shows that such concessions to expediency as the use of an average or approximate value of p and the retention of the original value of β with the revised values of a, b, and c are fully justified in this case.

7. IMPORTANCE OF SUITABLE CHOICE OF REFERENCE TEMPERATURE AND SECOND TEMPERATURE FOR COMPENSATION OVER A WIDE RANGE OF TEMPERATURE

In instruments for special applications such as on airplanes, relatively large ranges of temperatures are encountered. For example, the standard upper and lower limits of temperature for the testing of airplane instruments are +45° C and —35° C, respectively. For such wide ranges the choice of suitable values of t_1 and t_2 becomes important, as may be shown by an extension of numerical example *1*. Curve *I* of figure 17 shows the departure from compensation of the millivoltmeter of this example for the extreme temperature range —40° to +50° C, computed for the original $t_1=20°$ and $t_2=30°$. The defect is practically all of one sign, that is, the indication of the millivoltmeter will be too low for all temperatures below 20° and above 30°, and the maximum error (at —40°) is 0.45 percent. It is very evident that the above reference temperatures are too close together and too far from the center of the temperature range. One way to reduce the magnitude of the maximum defect in compensation is to increase the strength of the magnetic field by about 0.22 percent, thus lifting curve *I* to form curve *II*. This halves the maximum error but the curve is still of undesirable form. Approximately the maximum positive defect in compensation exists over the range

0 to 50°, and the change from this value to an equally large negative defect at −40° occurs at an increasing rate as the temperature decreases from 0°. A better choice of reference temperature and second temperature is $t_1 = -20°$ C and $t_2 = +30°$ C. Curve *III* shows the resulting defect in compensation for the mechanism and the requirements of example *1* with the values of a, b, c, and β revised as required by the new basic temperatures. The maximum defect in compensation is now 0.14 percent at −40°. The maximum positive defect is 0.055 percent and occurs near +5° C. Curve *IV* shows that by "lifting" curve *III* by 0.44 percent the departure from exact compensation may be kept just within the limits ± 0.1 percent over the whole of this large range of temperature, which is a strikingly

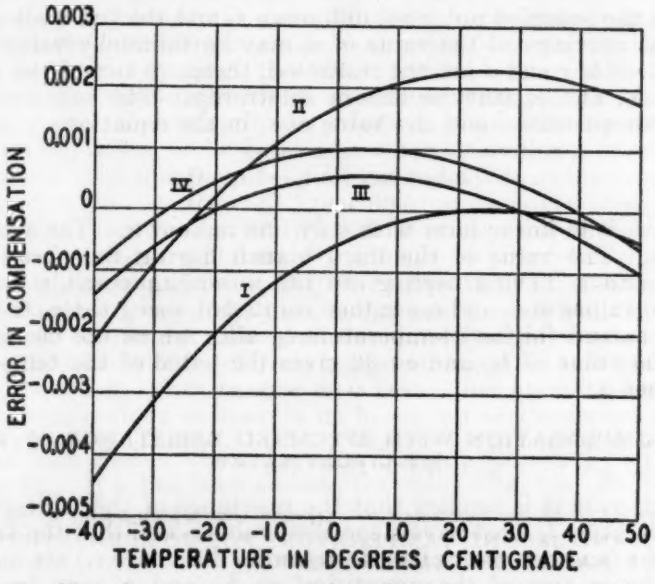

FIGURE 17.—*Error in compensation of the millivoltmeter of example 1 when used over a very wide range of temperature.*

Curve *I* is for the original case of t_1 and t_2=20 and 30° C, respectively. Curve *II* is equivalent to curve *I* "lifted" to equalize the + and − errors. Curve *III* is for new values $t_1 = -20°$ C and $t_2 = +40°$ C. Curve *IV* is curve *III* lifted to equalize the + and − errors. It is the curve which would apply to the case of $t_1 = -28.3°$ C and $t_2 = +40.5°$ C.

good performance. It shows that although the defect in compensation of a Swinburne-compensated millivoltmeter is necessarily a nonlinear function of temperature the defect may be kept within narrow limits by suitable choice of the reference temperature and the second temperature.

It will be noted that curve *IV* crosses the line of zero departure at about −28.3° and +40.5° C. These temperatures were taken as t_1 and t_2, respectively, and the data for a curve were computed. The values of defect in compensation agreed so closely with those of curve *IV* that it was not feasible to plot them as a separate curve.

To sum up: the mean of t_1 and t_2 should be near the center of the range of temperature to be covered, and the best values of t_1 and t_2 may be found by first assuming a pair of values, computing the

corresponding curve, "lifting" it to make the maximum positive departure equal numerically to the maximum negative departure, and then finding the best values of t_1 and t_2 from the intersection of the lifted curve with the line of zero departure from exact compensation. The values of a, b, c, and β should then be computed for these basic temperatures.

VII. COMPENSATION OF A MILLIVOLTMETER WHEN SOME QUANTITIES ARE SPECIFIED AND THE OTHERS MAY BE CHOSEN ARBITRARILY

1. COMPENSATION WITH SPECIFIED FULL-SCALE POTENTIAL DIFFERENCE

From the specified potential difference e_f and the full-scale current i_{f1} in the moving coil the value of s_1 may be found by using eq 15. The values of r and d are not restricted, therefore two of the quantities a_1, b_1, and c_1 may be chosen arbitrarily. The substitution of these two quantities and the value of s_1 in the equation

$$a_1b_1+a_1c_1+b_1c_1-b_1s_1=0 \tag{17}$$

will leave it in linear form with only one unknown. The solution is obvious. The value of the third branch having thus been found, and a_1 and c_1 having been given the minimum possible values of α and γ, values of a_2 and c_2 are then computed, using these coefficients for the second (higher) temperature t_2, after which the use of eq 29 gives the value of b_2, and eq 30 gives the value of the temperature coefficient β.

2. COMPENSATION WITH SPECIFIED RESISTANCE OF THE MILLIVOLTMETER

In this case it is implied that the resistance of the millivoltmeter at temperature t_1 must have a specified value r_1 and that the values of d and of s (and hence of full-scale potential difference e_f) are unimportant. Again two of the quantities, a_1, b_1, and c_1 may be chosen arbitrarily. They are to be substituted, with the value of r_1, in eq 19, namely,

$$a_1b_1+a_1c_1+b_1c_1-a_1r_1-b_1r_1=0 \tag{19}$$

and the resulting linear equation is then to be solved for the third unknown. The procedure for finding the values of b_2 and β is the same as that given for the preceding case.

3. COMPENSATION WITH SPECIFIED TOTAL DAMPING RESISTANCE

In the case it is implied that the total damping resistance at temperature t_1 must have a specified value d_1 and that the values of r and s are unimportant. As in the two preceding cases, any two of the values of a_1, b_1, and c_1 are chosen. With the prescribed value of d_1 they are substituted in eq 21, namely,

$$a_1b_1+a_1c_1+b_1c_1-b_1d_1-c_1d_1=0 \tag{21}$$

and the resulting linear equation is then solved for the remaining unknown. The procedure for finding b_2 and β is the same as in the two preceding cases.

4. COMPENSATION WITH SPECIFIED FULL-SCALE POTENTIAL DIFFERENCE AND SPECIFIED RESISTANCE OF THE MILLIVOLTMETER

In this case only one of the values of a_1, b_1, and c_1 may be chosen arbitrarily. The equations relating to this case are

$$a_1b_1+a_1c_1+b_1c_1-b_1s_1=0 \tag{17}$$

$$a_1b_1+a_1c_1+b_1c_1-a_1r_1-b_1r_1=0 \tag{19}$$

from which it follows that

$$a_1r_1+b_1r_1-b_1s_1=0 \tag{82}$$

$$b_1=\frac{a_1r_1}{s_1-r_1} \tag{83}$$

$$a_1=\frac{b_1(s_1-r_1)}{r_1} \tag{84}$$

If a_1 has been arbitrarily chosen, the value of b_1 is given explicitly by eq 83, and c_1 is found by using a relation derived from eq 17 and 83, namely,

$$c_1=\frac{r_1s_1-a_1r_1}{s_1} \tag{85}$$

If b_1 has been chosen, the value of a_1 is given directly by eq 84 and c_1 by eq 85. If c_1 has been chosen, the value of a_1 may be found by using the formula, derived from eq 85,

$$a_1=\frac{s_1(r_1-c_1)}{r_1} \tag{86}$$

after which the value of a_1 is substituted in eq 83 to get the value of b_1. The values of b_2 and β are then computed as in the preceding cases.

5. COMPENSATION WITH SPECIFIED FULL-SCALE POTENTIAL DIFFERENCE AND SPECIFIED TOTAL DAMPING RESISTANCE

Here also only one of the quantities a_1, b_1, and c_1 may be chosen arbitrarily. The appropriate equations are

$$a_1b_1+a_1c_1+b_1c_1-b_1s_1=0 \tag{17}$$

$$a_1b_1+a_1c_1+b_1c_1-b_1d_1-c_1d_1=0 \tag{21}$$

from which it follows that

$$b_1d_1+c_1d_1-b_1s_1=0 \tag{87}$$

$$b_1=\frac{c_1d_1}{s_1-d_1} \tag{88}$$

$$c_1=\frac{b_1(s_1-d_1)}{d_1} \tag{89}$$

If b_1 is the arbitrarily chosen quantity, the value of c_1 is given directly by eq 89, and if c_1 is given, b_1 is found by using eq 88. In either case the value of a_1 is found by the use of a relation derived from eq 17 and 88, namely,

$$a_1=\frac{d_1(s_1-c_1)}{s_1} \tag{90}$$

If a_1 is chosen, c_1 may be found from a relation derived from eq 90, namely,

$$c_1=\frac{s_1(d_1-a_1)}{d_1} \tag{91}$$

after which the value of b_1 is to be found by the use of eq 88. The values of b_2 and β are then to be computed as in the preceding cases.

6. COMPENSATION WITH SPECIFIED RESISTANCE OF THE MILLIVOLTMETER AND SPECIFIED TOTAL DAMPING RESISTANCE

The basic equations applying to this case are

$$a_1b_1+a_1c_1+b_1c_1-a_1r_1-b_1r_1=0 \tag{19}$$

$$a_1b_1+a_1c_1+b_1c_1-b_1d_1-c_1d_1=0 \tag{21}$$

Any one (but only one) of the quantities a_1, b_1, and c_1 may be chosen arbitrarily, after which eq 19 and 21 may be solved for the other two. The solution yields two pairs of roots. According to the relative magnitude of the arbitrarily chosen quantity, one pair or both pairs may lead to physically possible values of resistance or to negative or imaginary values which cannot be realized. When both pairs of roots lead to positive real values of resistance there may be a large difference in matters of performance in the two cases, such as the full-scale potential difference or the fractional part of the current which is bypassed around the moving coil and produces no torque. There are three cases.

Case 1.—Let a_1 be chosen arbitrarily. The solution of eq 19 for b_1 is

$$b_1=\frac{a_1(r_1-c_1)}{a_1+c_1-r_1} \tag{92}$$

The substitution of this value of b_1 in eq 21 gives a quadratic equation in c_1 of which the solution is

$$c_1=\frac{r_1\pm[r_1^2-4a_1r_1(d_1-a_1)/d_1]^{\frac{1}{2}}}{2} \tag{93}$$

Each of the two values of c_1, substituted in eq 92 with the chosen value of a_1, gives a corresponding value of b_1. Note that the value of b_1 corresponding to one of the values of c_1 is not applicable with the other value of c_1.

Case 2.—Let b_1 be chosen arbitrarily. The solution of eq 19 for a_1 is

$$a_1=\frac{b_1(r_1-c_1)}{b_1+c_1-r_1} \tag{94}$$

The substitution of this value of a_1 in eq 21 gives a quadratic equation in c_1 of which the solution is

$$c_1=\frac{r_1-2b_1\pm[(r_1-2b_1)^2-4b_1(b_1-r_1-b_1r_1/d_1)]^{\frac{1}{2}}}{2} \tag{95}$$

Each value of c_1, substituted in eq 94 with the chosen value of b_1, gives a corresponding value of a_1. Each value of a_1 is applicable only with the value of c_1 which gives rise to it.

Case 3.—Let c_1 be chosen arbitrarily. The quadratic equation of case *1* may be rearranged with a_1 as the unknown. The solution is

$$a_1=\frac{d_1\pm[d_1^2-4c_1d_1(r_1-c_1)/r_1]^{\frac{1}{2}}}{2} \tag{96}$$

Each of these two roots, substituted in eq 92 with the chosen value of c_1, gives the corresponding value of b_1.

In each of these three cases the solution is to be completed by finding the minimum possible values of α and γ, computing from them values of a_2 and b_2 for the desired higher temperature t_2, determining b_2 by eq 29, and finally determining β by eq 30. The minimum possible values of α and γ are obtained by making the coil a'' and all (or as much as possible) of the c branch of manganin.

VIII. EXPERIMENTAL PROCEDURES FOR ROUTINE COMPENSATION OF INSTRUMENTS OF A GIVEN TYPE

1. NECESSITY FOR AND PREPARATIONS FOR THE EXPERIMENTAL PROCEDURES

In the routine manufacture of millivoltmeters of a given type to meet identical requirements it is an economic necessity to have simple and rapid methods. Such methods are proposed in outline here in the hope that they may at least suggest feasible procedures to those who (unlike the author) are in direct touch with the problems of instrument manufacture.

If each millivoltmeter were to be compensated individually in accordance with the appropriate formulas of this paper, the following data would have to be determined for it experimentally: resistance a' of the moving coil and current i_f for full-scale deflection at two

accurately known temperatures, and the total resistance d for the kind of damping desired. To determine the values of a'', b, c, and β would require calculations for each instrument.

In preparation for the proposed more practical and expeditious experimental procedures the above detailed process would be carried out for a sufficient number of instruments to obtain good average values of a, b, and c. Thereafter, each millivoltmeter mechanism would be subjected to certain tests in a controlled-temperature enclosure having a window through which the indication could be accurately observed. Such an enclosure is indicated diagrammati-

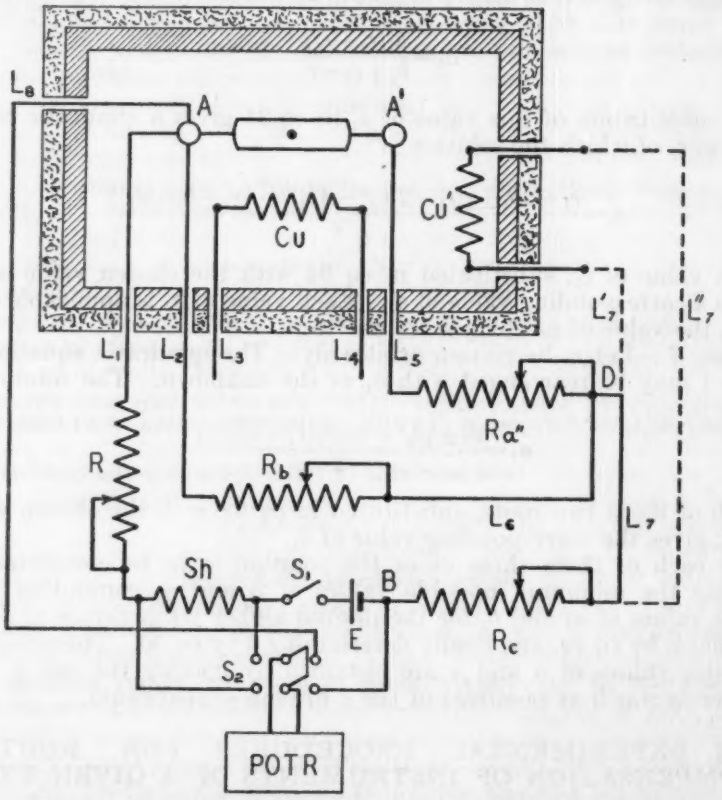

FIGURE 18.—*Experimental method of millivoltmeter compensation.*

The mechanism and copper coils *Cu* and *Cu'* are in a controlled-temperature enclosure. Manganin rheostats $R_{a''}$, R_b, and R_c serve as temporary a'', b, and c coils, respectively. A cell E supplies a current which can be regulated by the rheostat R and measured by the potentiometer and shunt *Sh*.

cally in figure 18. Manganin leads L_2 and L_5 are brought out from the ends A and A' of the moving coil[23] and similar leads L_3 and L_4 are brought out from the ends of a copper coil *Cu*. Three manganin rheostats $R_{a''}$, R_b, and R_c are used as temporary a'', b, and c coils, respectively. It is necessary that these rheostats be capable of fine adjustment, say to 0.01 ohm or finer. Ordinary precision rheostats do not usually have such small steps. The use of the Waidner-

[23] That is, from the outer ends of the springs which conduct the current to and from the moving coil.

Wolff [24] adjustable resistance element makes such steps, and even much finer ones, entirely feasible. Rheostats composed of such elements, adjustable in steps of say 0.001 ohm, are essential for the rapid and accurate performance of the necessary tests. The leads L_2 to L_5 inclusive are preferably adjusted to convenient round values of resistance which have to be taken into account.[25] The copper coil *Cu* is wound on a metal spool which is mounted in close thermal proximity to the moving coil, as it will be in the final assembly of the instrument, but it is given a resistance say 10 percent larger than the value which experience indicates will be finally required. Its use in the manner described below makes it unnecessary that the temperature during the tests within the enclosure should have exactly the specified values t_1 and t_2, or that the nominal increase of temperature t_2-t_1 within the enclosure should either have the specified value or be accurately known, or that the temperature coefficient of resistance of the particular copper wire should be known. The leads L_1 and L_8 may be of copper wire small enough to prevent any significant rate of conduction of heat. Their resistances are immaterial. The leads L_6 and L_7, not being in the temperature enclosure, should be of copper and of negligible resistance. The alternative leads L_7' and L_7'', shown by dotted lines in figure 18, should be of manganin, and the coil *Cu'* which they put in circuit (on occasion) between the point *D* and the rheostat R_c should be of copper. This coil should be wound on a card or be otherwise constructed so as to assume the temperature of the surrounding air in a relatively short time, and it need not be mounted on the mechanism. This coil and the alternative leads are used when the millivoltmeter is to be calibrated to measure the potential difference between the ends of a pair of leads connected to its terminals. In the following discussion it is assumed that the lead L_7, shown as an unbroken line, is used unless otherwise specified.

Although the general experimental procedure is believed to be adaptable to all of the cases treated analytically in the preceding section, it is thought sufficient to outline specific procedures for only selected cases.

2. EXPERIMENTAL PROCEDURE FOR SPECIFIED FULL-SCALE POTENTIAL DIFFERENCE AND SPECIFIED RESISTANCE OF THE MILLIVOLTMETER

The rheostat R_a'', figure 18, is set to make the sum of its resistance and that of the moving coil and the lead L_5 equal to the previously determined average value of a_1. The temperature within the enclosure is held at or close to the reference temperature t_1 until the temperature within the millivoltmeter mechanism is constant, as shown by the constancy of the resistance of the copper coil *Cu*. The value of this resistance is recorded. The switch S_1 is then closed and the rheostat *R* is adjusted until the current measured by the potentiometer and the shunt *Sh* has the value e_f/r, where e_f and r are the specified full-scale potential difference and the specified resistance of the millivolt-

[24] J. Research, NBS **15**, 477, (1935) RP842.

[25] If L_4 to L_8 were of copper, subsidiary measurements would have to be made on a pair of similar "dummy" leads extending into the enclosure and having their inner ends joined together. It would not answer the purpose to make these leads of heavy copper wire to make the resistance negligible, because such leads would conduct too much heat. Manganin has only one-twentieth of the thermal conductivity of copper.

meter. The rheostat R_b is then adjusted to give full-scale deflection, the current being kept constant meanwhile by readjustment of R. The resistance of R_b is then recorded; with the resistances of L_2 and L_6 added, it gives the value of resistance b_1 which the final b coil must have at this temperature (approximately t_1). The value of the resistance R_c up to this time is immaterial. The potentiometer is then connected to measure the potential difference between the points A and B, and this potential difference is regulated by the rheostat R while the rheostat R_c is adjusted until the specified full-scale potential difference produces full-scale deflection. If the millivoltmeter is to indicate the difference of potential between its own terminals, the resistance of R_c plus that of L_7 equals the resistance which the final c coil should have at reference temperature. If the millivoltmeter is to indicate the difference of potential between the ends of a pair of copper leads attached to its terminals, the procedure just outlined would differ only in that the lead L_7 would be removed and its place taken by the manganin leads L_7' and L_7'' and the coil Cu', this coil having a resistance equal to that of the pair of leads. In this case, the sum of the resistances R_c, L_7', and L_7'' equals the resistance to which the final manganin c coil should be adjusted.

The determinations at approximately reference temperature t_1 having been completed, the temperature within the enclosure is then raised to approximately t_2 and held until the resistance of the coil Cu becomes constant. The value of this resistance is recorded. The switch S_1 is then closed, R_a'' and R_c are left undisturbed, and the resistance of R_b is increased to make full-scale deflection again correspond to the specified potential difference[26] between A and B. The increment Δb in the resistance of R_b is the amount by which the copper coil, which is to form part of the final b branch, must increase for the given increase in temperature. Because the resistance of the coil Cu was made a little larger than necessary, its observed increase in resistance ΔCu will be somewhat larger than Δb. The resistance of the coil Cu must be reduced so that the portion remaining, if it had been in the enclosure, would have shown a change in resistance equal to Δb; that is, its resistance must be made $\Delta b/\Delta Cu$ times its original value. The temperature at which this relative reduction in resistance is made is immaterial.[27] The coil is then to be remounted within the mechanism, one of its terminals is to be connected to the point A, and the manganin coils a'' and c are to be mounted and connected, all as shown in figure 1, but with the b branch as yet incomplete. A suitable finely adjustable rheostat, for example, R_a'' of figure 18, is used to close the gap in the b branch temporarily, and is adjusted until the specified potential difference e_f gives full-scale deflection at approximately reference temperature.[28] A manganin coil having a

[26] A slight shift of zero is sometimes caused by raising the temperature of the mechanism. When this occurs, and the zero adjuster is inaccessible, allowance should be made for the shift so that the net angular deflection is the same at t_2 and t_1.

[27] It is difficult to adjust a copper coil accurately. The author places the coil, which is wound on a brass spool, on a massive metal block which rests on the bottom of a thick-walled cast-aluminum vessel having a cover of the same material. Manganin leads of known resistance are brought out from the ends of the coil to a bridge. One junction of a thermocouple is clamped to the massive metal block and the other is in an ice bath. The aluminum vessel is surrounded by heat-insulating material contained in a box. Suitable means are provided for holding the temperature of the vessel at desired values.

When the resistance of the coil at a definite temperature has been measured, the coil is removed and adjusted by measuring with the bridge the resistance *of the small margin to be removed*. A given relative error in this measurement affects the resistance of the finished coil to a much smaller extent than it would if the measurement were made directly on the part which is to form the finished coil.

[28] It is not necessary that this test should be made at exactly the first temperature (approximately t_1) used in the test within the enclosure, nor that the millivoltmeter should be in the enclosure. The test might be made equally well at or near the second temperature used in the test within the enclosure.

resistance equal to that to which this rheostat was adjusted during this test, plus the resistance of the necessary connecting leads used, is then mounted in the millivoltmeter and connected to complete the b branch and consequently the electrical network of the millivoltmeter.

3. EXPERIMENTAL PROCEDURE FOR SPECIFIED FULL-SCALE POTENTIAL DIFFERENCE AND SPECIFIED TOTAL DAMPING RESISTANCE

In this case, at reference temperature, $R_{a''}$ and R_b are set to make the resistances of the corresponding arms equal to the predetermined average values. The potential difference between the points A and B is then brought to the specified full-scale value while R_c is adjusted to give full-scale deflection. The switch S_1 is then opened, A and B are joined [29] by a wire of negligible resistance, the lead L_5 is disconnected from $R_{a''}$ and a bridge or an ohmmeter is connected in the gap so formed to measure the actual value of total damping resistance. If this resistance is too large, for example, the resistance of R_c is reduced by a small amount and R_b is reduced until the specified potential difference again produces full-scale deflection. The measurement of total damping resistance d is then repeated. After a few trials, with values of d recorded as a function of R_c, interpolation will give with sufficient accuracy the value of c to produce the desired value of d.

The rest of the procedure, at the higher temperature t_2, is the same as in the preceding section.

It is assumed in the above method that the mechanism is received for this test with a specified value of d which has been experimentally determined for it. If damping caused by pivot and air friction be neglected, the value of d, in instruments nominally identical, will vary directly as the square of the magnetic flux density in the air gap and inversely, as the square root of the spring strength. In the next section the variation in d resulting from manufacturing variations in the strength of the magnets will be taken into account.

4. EXPERIMENTAL PROCEDURE FOR SPECIFIED FULL-SCALE POTENTIAL DIFFERENCE, SPECIFIED RESISTANCE OF THE MILLIVOLTMETER, AND SPECIFIED TOTAL DAMPING RESISTANCE OF AN INSTRUMENT OF NORMAL STRENGTH OF MAGNET

It is assumed in this case that each millivoltmeter mechanism is received for test with specified values of e_f and r; that the strength of the magnets will vary from the average value and that no magnetic shunt is used to bring the field strength to the standard value; that the variation in the strength of the springs, among different instruments, is small enough to be disregarded; and that the damping is to be the same as that of an instrument of normal field strength having a total damping resistance d. A given relative variation in field strength of individual mechanisms will cause the same relative variation in the sensitivity resistance s, and for a given value of s there is a unique set of values of a, b, and c. Such sets of values may be computed, by means of eq 22 to 24, for values of s over a suffi-

[29] To make the point A accessible for this purpose, the greater part of the lead L_5 may be made of copper wire large enough to make its resistance negligible, and only the short piece which enters the enclosure may be of finer wire.

cient range to take care of manufacturing variations and with values of d which vary as the square of s. Values computed on this basis

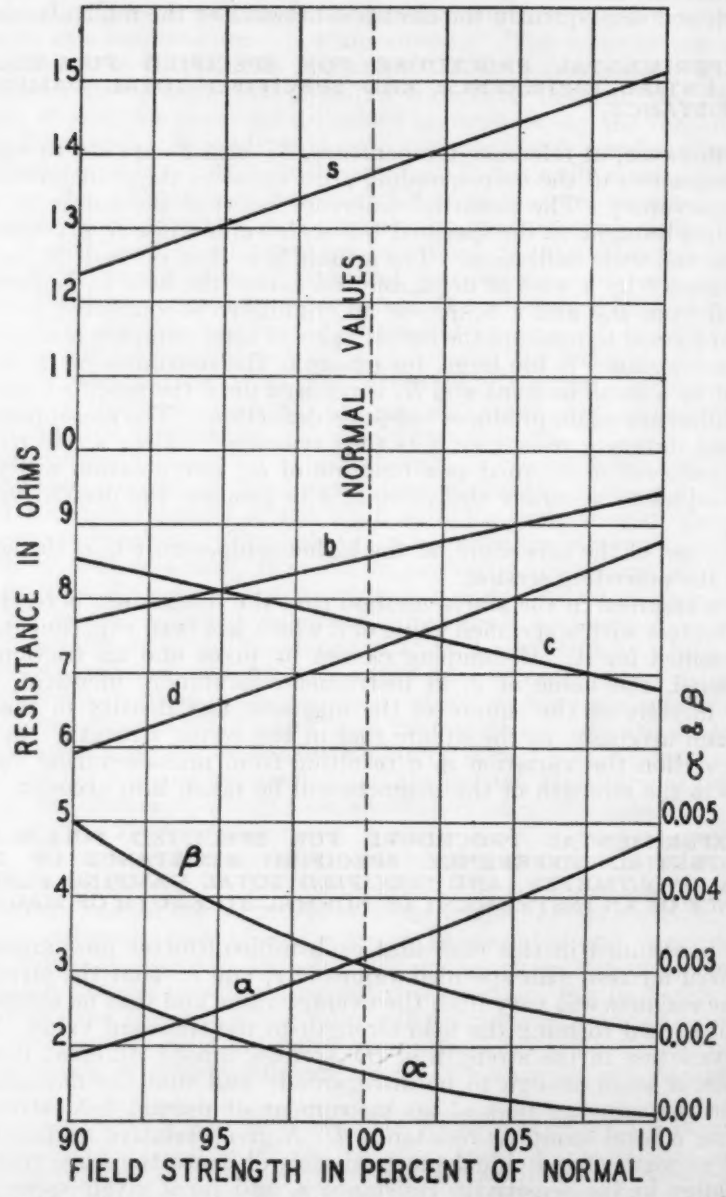

FIGURE 19.—*Curves showing the manner in which the resistances a, b, c, and d and the temperature coefficients α and β must vary to maintain specified values of e_f and r and a specified degree of damping for a range of values of strength of magnetic field between 0.9 times normal value and 1.1 times normal value.*

for the millivoltmeter mechanism of example *1* are shown in figure 19. It may be seen that if the sensitivity of a given mechanism is

higher than normal (that is, the current in the moving coil for full-scale deflection is less than normal) it is necessary to increase a and b and decrease c. The converse statements apply when the sensitivity resistance is below the normal value.

The mechanism under test having been in the enclosure (fig. 18) at approximately reference temperature t_1 until the resistance of the coil Cu is constant, the resistance of R_b is made infinite, that of $R_{a''}$ is made zero, the switch S_1 is closed, and R and R_c are varied until the potential difference between A and B has the specified value and the pointer is deflected to the full-scale mark. The switch S_1 is then opened and the resistance from A to B is measured. With this experimentally determined value of s the curves of figure 19 are used to find the appropriate values of a, b, and c. $R_{a''}$, R_b, and R_c are then set to give the corresponding branches these values. Full-scale potential difference is then applied between A and B as a check, after which the resistance r between these points may be measured. The total damping resistance d may be checked by short-circuiting the instrument across the terminals A and B, opening the connection between L_5 and $R_{a''}$, and inserting an ohmmeter or a bridge in the gap so formed.

The rest of the procedure, at the higher temperature t_2, is the same as in the two preceding sections.

5. EXPERIMENTAL PROCEDURE FOR LOCATING THE VOLTMETER TAP POINT

It is suggested, on the basis of the author's limited experience, that it will probably be sufficient to determine the location of the voltmeter tap point for a moderate number of instruments of a given model, and thereafter to use the average location of this point for all such instruments.

The determination of the voltmeter tap point is to be made with the mechanism in the controlled-temperature enclosure after the values of a_1, b_1, and c_1 have been found for the millivolt range. The connections are as shown in figure 20. The rheostat R_c is connected in series with $R_{a''}$ and one terminal of the supply cell E is connected to the junction T of $R_{a''}$ and R_c. This junction is thus a tap point on the a'' branch of the network, and the procedure is to vary the resistance in these two rheostats while the sum of their resistances is kept constant at the value which $R_{a''}$ had in the test of the given mechanism as a millivoltmeter. This procedure is equivalent to sliding the point T along the a'' part of the a branch, and in fact, a slide wire could be used for this purpose if means could be provided for conveniently bringing its entire resistance to the value which $R_{a''}$ had when the mechanism was tested as a millivoltmeter.

To avoid the taking of unnecessary observations the average location of the tap point in similar instruments previously tested should be known, and the rheostats $R_{a''}$ and R_c should be set initially to reproduce this condition. With the mechanism at or near reference temperature the switch S is closed and the rheostat R is adjusted to give full-scale deflection of the mechanism under test. The magnitude of the current I_1 is then recorded, the resistance of $R_{a''}$ is increased and that of R_c is decreased by the same amount to produce the effect of shifting the tap point T by say 5 percent of a'', and the

new value of I is recorded. The process is repeated after T has been set to give a 10-percent shift in the same direction and then shifts of 5 percent and 10 percent in the opposite direction from the initial position. The temperature of the mechanism is then raised to approximately t_2 and the resistance of R_b is then raised to the value appropriate for this temperature, as shown by the previous test for compensation as a millivoltmeter, after which the values of the current I are measured for the five positions of T previously used. The five values I_1 at temperature t_1 are plotted in a curve as a function of pa'', that is, of the resistance of R_c, and the five values I_2 at temperature t_2 are plotted to the same coordinates as a second curve. The

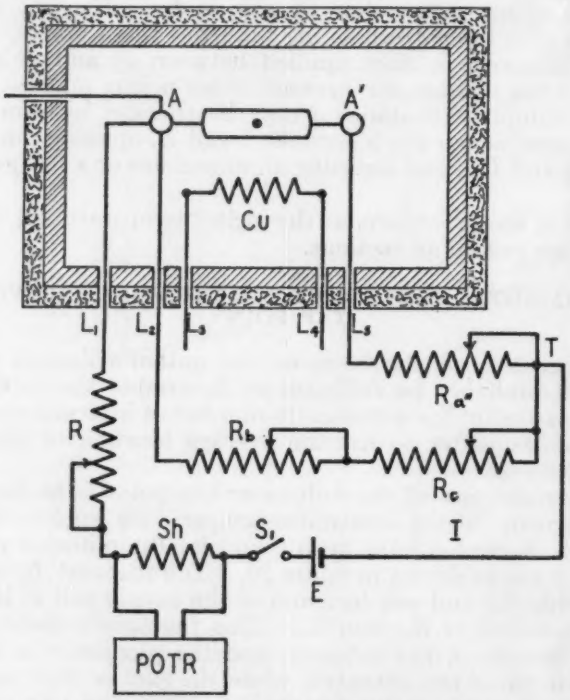

FIGURE 20.—*Experimental method of locating the voltmeter tap point.*

The mechanism and a copper coil *Cu* are in a controlled-temperature enclosure. The manganin rheostat R_b serves as a temporary b branch while $R_{a''}$ and R_c in series serve as a temporary a'' coil. By varying R_a and $R_{c''}$ while keeping their sum constant the effect of moving the tap point T along the a' coil is obtained.

abscissa of the point of intersection of these two curves is the value which pa'' should have for volt ranges in which the proportion of copper to manganin is so small that the current for a constant applied voltage may be regarded as constant over the working range of temperature. It will be seen from the values of n and p for example *2*, p. 527, that p for that case changes only 3 percent for volt ranges from 1.5 to 1,500 volts. Furthermore, a degree of temperature compensation adequate for practical purposes when the limited accuracy of reading the deflection is considered, may be obtained with only a moderately accurate value of p. For instance, in example *3*, p. 529, in which p=0.9965 for $n=\infty$, the use of $p=0.75$ causes a defect in

compensation of only 0.1 percent when the temperature is increased from 20 to 30° C.

6. EXPERIMENTAL PROCEDURE FOR DETERMINING THE EFFECT ON THE COMPENSATION OF MANUFACTURING VARIATIONS OF MILLIVOLTMETER CONSTANTS FROM THEIR AVERAGE VALUES

After a number of millivoltmeters have been compensated by the process of accurately measuring their constants and computing appropriate values, it would save much expense thereafter if subsequent instruments could be given the values of a, b, c, and β which had been found to apply to the average instrument. It is desirable, before doing this, to ascertain the effect on the compensation of the manufacturing variations in certain constants of the instruments. For simplicity, let it be assumed that each mechanism in question has a magnetic shunt by means of which s can be brought to the standard value. The constants which will vary from one instrument to another, and on which a sufficient number of values should be observed, are $a_1'\alpha'$, $b_1\beta$, and δ. The quantity $a_1'\alpha'$ is the increase in resistance, in ohms, of the moving coil and springs for an increase of 1° above the reference temperature, and a knowledge of its value makes it unnecessary to know its components a_1' and α', both of which may vary in opposite directions without affecting the performance, if their product remains unchanged.

The test may be made for convenience in the temperature-controlled enclosure of figure 18. With the rheostats $R_{a''}$, R_b, and R_c set to give the standard values, S_1 closed and R adjusted to give full-scale deflection, $R_{a''}$ is changed by the amount of $(t_2-t_1)\Delta a_1'\alpha'$, where t_2-t_1 is the standard temperature interval and $\Delta a_1'\alpha'$ is the largest observed departure in $a_1'\alpha'$ from its average value. The resulting displacement of the pointer from the full-scale mark will be the error of compensation which would be caused by this maximum value of $\Delta a_1'\alpha'$ if the instrument were to be equipped with coils of the standard values. Similarly, if it is known that in a number of copper b coils, the resistances of which to produce compensation have been determined experimentally or by computation, the maximum variation from the mean value of Δb has a given value, the effect of this variation may be found in the same manner as that of $\Delta a_1'\alpha'$. The effect of the maximum variation $\Delta\delta$ of the coefficient δ from its average value needs no experiment and is simply $(t_2-t_1)\Delta\delta$. Finally, the greatest possible defect in the compensation, under the most unfavorable conditions, may be had by adding the observed effects of the three variations.

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TIME FACTORS IN THE IONIZATION OF CARBON DISULPHIDE BY X-RAYS

By Lauriston S. Taylor

ABSTRACT

The conductivity of CS_2 exposed to X-rays varies with the time of application of voltage and time of exposure. It is shown that the various phenomena observed can be explained by barrier potentials due to space charge. Effects with X-rays appear to differ only in degree from those observed without X-rays. At direct-current fields of 70 kv/cm the conductivity had reached about 75 percent of its saturation value. Measurement of the barrier potential showed it to be linear with applied potential; to decrease with increase in radiation intensity; and to vary from 40 to 60 percent of the applied voltage. Current-decay curves obey a simple power law, the power of time changing very slowly with field strength within a given time interval. Square-wave voltage was applied to the cell and short interval current measurements made under essentially direct-current conditions. Current-decay curves for intervals as small as 0.004 sec follow out those made for longer times, but show a sharp increase at about 0.02 sec due probably to sweeping out the initial ions formed in a field-free cell.

Reciprocal plots of ionization current against voltage show the same linearity at high fields as reported previously. Such plots obtained with direct-current or square-wave voltage extrapolate to the same point for $1/V=0$, from which the saturation current may be derived. Using this method, saturation conditions were studied for several types of ionization chamber with different X-ray intensities and qualities. The application of this work to the problem of radiation measurements is discussed briefly, and, in a large measure, it verified our earlier work carried out in less detail.

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I. INTRODUCTION

Various workers have studied the conductivity effect of ionizing radiations on highly insulating dielectric liquids. Among the earliest work was that of Jaffé[1] and his students,[2] who studied the effects of alpha rays and gamma rays on a number of liquids, including carbon disulphide, carbon tetrachloride, and hexane, and explained the current-voltage curves by the theory of columnar ionization.

There are definite dissimilarities between the ionization produced by X-rays in liquids and gases. In liquids the ions are concentrated in densely populated groups or columns within which the recombination rate is very high. As a result of this, the fields normally used to withdraw all the ions produced in a gas (200 v/cm), furnish a measured ionization current which, in liquids, is only a small fraction of the saturation current. Also, electrical breakdown of a strongly ionized liquid occurs at field strengths far below saturation current conditions. A further important difference is that various complicated time effects are involved in the ionization of liquids, so that the measured current depends upon the time lapsed after application of voltage and radiation. These time effects were first noted by Jaffé[3] for liquids exposed to radiation and later studied in considerable detail by Whitehead and Marvin[4] for transformer oils at moderate field strengths but not exposed to radiation. Recent tests of Jaffé's theory have been made by Mohler and Taylor,[5,6] Zanstra,[7] and Clay and van Tijn.[8] Also Stahel[9] has constructed very small ionization chambers with which he has investigated the distribution of intensity of gamma-ray ionization produced in water phantoms. His work being concerned only with relative intensity measurements, he used comparatively low field strengths.

Jaffé's theory leads to the following relationship for the ionization current I_x at any field X:

$$\frac{I_\infty}{I_x}=1+\frac{\alpha N}{7.85duXf(X)},$$

where α is the recombination coefficient; u the ion mobility; N, the density of ion pairs per centimeter of column length; and d, the column diameter. Since $f(X)$ is a complicated function, and not easily evaluated at the fields employed by Jaffé (5 kv/cm) this equation was not used to determine the saturation current. However,[10] $f(X)$ approaches 1 for applied fields in excess of about 10^4 v/cm and a plot of $1/I_x$ against $1/X$ approaches a straight line which can be extrapolated to give the reciprocal of the current at infinite fields. This method was successfully employed in the determination of the number of ions per quantum absorbed for liquid carbon bisulphide.

[1] G. Jaffé, Ann. Physik **42**, 331 (1913); Le Radium **10**, 126 (1913).
[2] H. J. van der Bijl, Verhandl. deut. phys. Ges. **15**, 102 and 210 (1913).
[3] G. Jaffé, Ann. Physik **25**, 257 (1908).
[4] J. B. Whitehead and R. H. Marvin, Trans. Am. Inst. Elec. Engrs. **49**, 649 (1930).
[5] F. L. Mohler and L. S. Taylor, J. Research NBS **13**, 659 (1934) RP733; Phys. Rev. **45**, 762 (1934).
[6] L. S. Taylor and F. L. Mohler, Sci. **81**, 318 (1935).
[7] H. Zanstra, Physica **2**, 817 (1935).
[8] J. Clay and M. A. van Tijn, Physica **2**, 825 (1935).
[9] E. Stahel, Strahlentherapie **31**, 582 (1929).
[10] See footnote 5.

The function $f(X)$ has also been evaluated by Zanstra [11] for gas under pressures ranging from 8 to 400 atmospheres.

There is further interest in the problem of ionization of liquids by radiation, from the point of view of its application to the comparison of X-ray and gamma-ray dosage in materials which approximate the physical properties of body tissue.[12]

In refining and extending the earlier measurements numerous interesting features developed, and it is the main purpose of this paper to discuss these features and their bearing upon the measurement of X-rays with liquid ionization chambers. Since the purpose of this work was to later apply the results practically, an endeavor was made throughout, to keep the technique as simple and inexpensive as possible.

II. LIQUIDS

It was desired that the liquids used have the following properties: (1) Low conductivity when not exposed to ionizing radiation; (2) a relatively large increase in conductivity when exposed to ionizing radiations; (3) effective atomic number, about that of water (7.5); (4) low viscosity; (5) density of about 1; and (6) low volatility (preferred but not positively essential.)

Of the various liquids tested [13] carbon bisulphide, ligroin, and tetrahydronaphthalene (tetralin) were most suitable. While ligroin and tetralin, having effective atomic numbers of about 6, were found better suited to the problem of radiation measurement, they had the disadvantage of showing a relatively small increase in conductivity, compared with CS_2, when exposed to X-rays. Consequently, CS_2 was used in the bulk of the exploratory work. It gave large ionization currents and was relatively easy to purify; however, the dark current was about 10 times that for ligroin and tetralin.

Some degree of purification of all the liquids was necessary and with CS_2 it was found that this could be attained without the more elaborate vacuum-distillation scheme used by us earlier.[14] Of primary importance was the removal of all traces of lint or dust suspended in the liquid. This necessitated all assembly and filling operations to be carried out within a dust-free hood.

In the early work, a reagent grade of CS_2 was passed about 10 times through the same filters of ordinary acid-free filter paper and thence into the ionization chamber. This process dried and cleaned the liquid with fairly satisfactory results. More recently, the CS_2 was refluxed with a reagent grade of P_2O_5, after which it was distilled directly into the cell. The cell was then placed under a bell jar which was thereupon exhausted to the point of producing mild boiling of the liquid, this serving to remove any gas bubbles or pockets. This method appeared to be at least as satisfactory as either vacuum distillation or refluxing with sodium.[15]

The lowest conductivity obtained with CS_2 was 7×10^{-16} mhos, and for tetralin, 5×10^{-17} mhos—measurements being made at 22 ° C, with a field strength of 60 kv/cm on a 1-mm layer, at least 15 min after application of a steady voltage.

[11] See footnote 7.
[12] See footnote 6.
[13] We are indebted to Dr. E. Wichers of the Chemistry Division of this Bureau for his assistance in searching for suitable liquids.
[14] F. L. Mohler and L. S. Taylor, J. Research NBS **13**, 659 (1934) RP733.
[15] We are indebted to Dr. R. T. Leslie, Research Associate, representing the American Petroleum Institute at this Bureau, for his assistance in trying various modes of purification.

III. IONIZATION CHAMBERS

The choice of ionization chamber was, in part, determined by the application of the problem to dosage measurement. In the first place, it was desired to measure the total number of ions per cubic centimeter produced in a layer not more than 1 mm thick at the surface of a liquid "phantom." Secondly, it was desired to keep as small as possible any corrections for absorption in or scattering from the ionization-chamber electrodes.

The two chambers shown in figures 1, 2, and 3 were used in most of the experiments. The chamber in figure 1 consists of a square fused-quartz plate with notches ground in the edges and about which two separate grids of 0.1-mm aluminum were woven. In the center is a hole 10 mm in diameter constituting, with the grids, the volume in which the ionization is measured. When used in this simple form in a broad X-ray beam there are relatively large stray ionization currents between the grids around the outside of the cell. Since these stray currents may not be proportional to the field strength, they should be eliminated in quantitative work; this was done somewhat crudely by means of mica and quartz shields mounted around the edges of the chamber.

In the chamber in figure 2, the electrodes were essentially embedded in a series of carefully ground fused-quartz rings, which in turn were

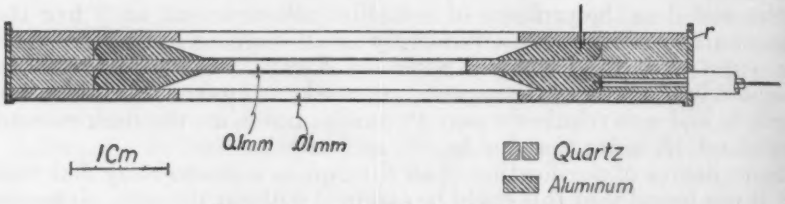

FIGURE 2.—*Completely shielded cell.*

held closely in position with a thin aluminum ring, *r*. The bottom of the cell was covered with 0.01-mm Al. The electrometer lead, supported on quartz beads, passed through a small aluminum tube which, together with the case, was grounded. It was thus impossible for any leakage current to reach the electrometer system except through the desired cell volume. The electrodes for this chamber could be either grids supported on perforated aluminum disks, figure 3, or solid aluminum disks. The latter were turned down at the center to a uniform thickness of about 0.1 mm and drilled with a number of 0.3-millimeter holes to facilitate removal of gas bubbles from the liquid. The use of undrilled plates was usually accompanied by unsteadiness of current at the higher field strengths because of small gas bubbles which could not escape.

The ionization chamber was placed in a shallow Pyrex dish of about 20-cc capacity. Leads extending through side tubes passed through grounded metal sleeves to avoid leakage. These tubes were plugged with tin, covered corks and sealed at the outer end with Duco cement. This cement was carefully tested in advance and found to be insoluble in the liquids used, as indicated by failure to affect the conductivity. Dried Cellophane cemented across the top of the dish made it satisfactorily airtight. The liquid to be used was

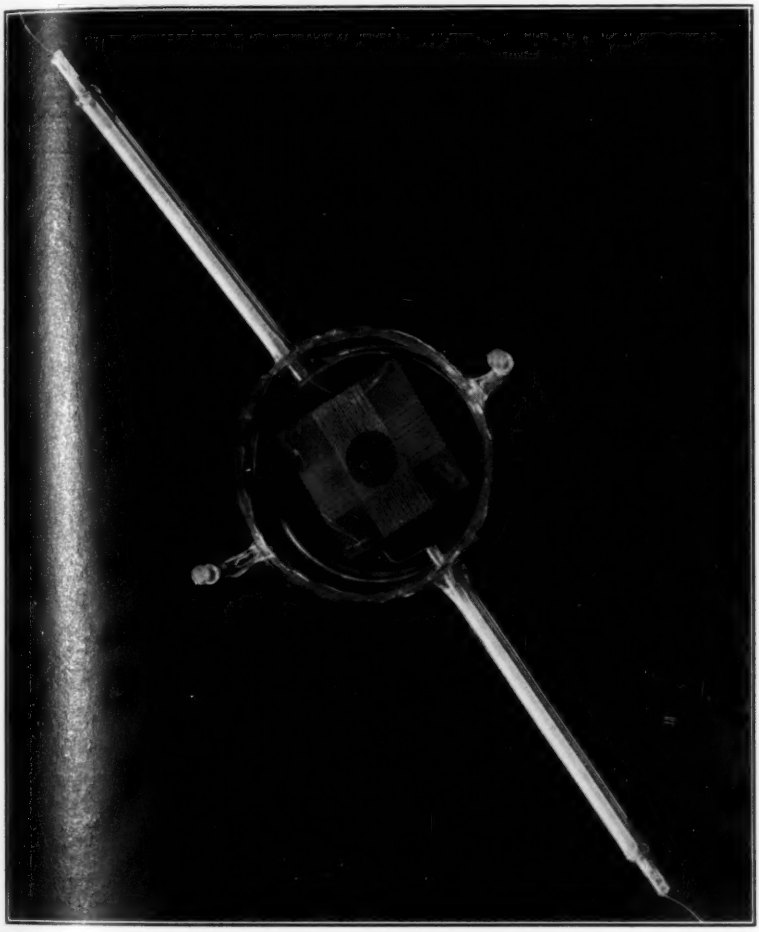

FIGURE 1.—*Square quartz-plate cell.*

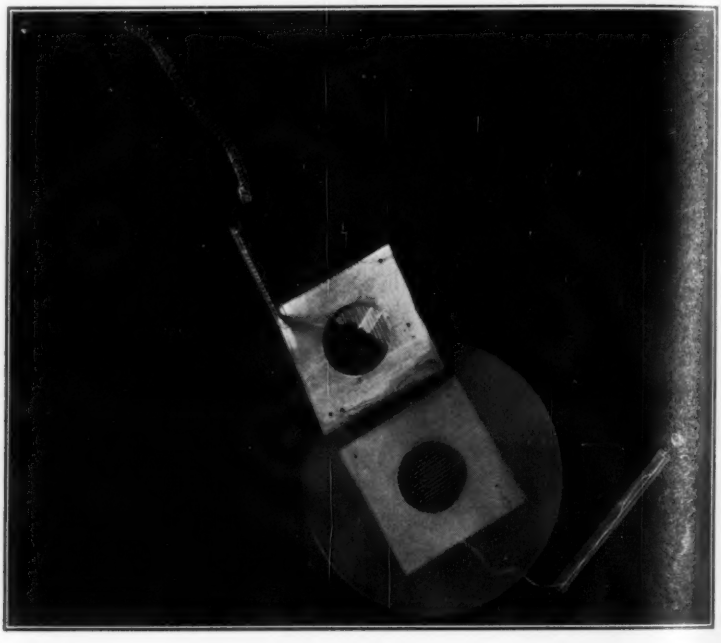

FIGURE 3.—*Aluminum electrodes for use in shielded cell.*

admitted through a short side tube after the whole assembly had been slowly baked for at least a day.

IV. RADIATION

X-rays of widely varying intensity and quality were produced by constant potential excitation in thick-walled air- or water-cooled tubes. The chamber was placed about 50 cm directly beneath the tube so that the beam passed through it normal to the plates. For comparison purposes the cell was used either imbedded in the surface of a large block of wax, or supported on a light cardboard platform essentially in free air. The X-ray beam was measured in roentgens per minute (r/min) by means of a calibrated thimble chamber.

V. IONIZATION CURRENT WITH DIRECT-CURRENT POTENTIAL

1. CURRENT-VOLTAGE CURVES

The shape of the current-voltage curve with the ionization chamber exposed to X-rays was first investigated. It was observed in Jaffé's studies,[16] that the steady current value at a given applied potential was reached somewhat gradually, and that after removal of the radiation the return to zero was likewise slow after the first large initial drop. In our earlier work [17] readings were taken 2 minutes after the radiation or the applied voltage was changed.

Figure 4 shows the typical performance of an ionization chamber (grid or plate type) under different conditions, the current being plotted as a function of the time. With the first application of voltage, the current rises almost instantly to a maximum and then decreases to an essentially steady value in about 10 minutes. This is repeated after each *increase* of voltage; but when the voltage is *decreased* instead, the opposite occurs—the current starts at a low value and slowly rises to a final steady value. To obtain the same steady-state current after an increasing or decreasing voltage, a lapse of 20 to 30 min is required between the change in voltage and the measurement.

Just before each voltage change in figure 4, the X-rays were shut off for about a minute, during which a reading of the "leakage" current was obtained. This leakage current was found to increase steadily with the applied voltage.

At the termination of the experiment, the voltage was cut off and the cell momentarily grounded. Upon reconnecting to the galvanometer, without applied voltage, a relatively large reverse current which decayed slowly to zero was observed. This action is, under similar conditions, typical of the various cells and liquids used.

Whitehead and his coworkers [18] [19] have obtained somewhat analogous results when transformer oils were subjected without X-rays to fairly high fields (10 kv/cm). He advanced the theory that the effects were due to large space charges made up of ion clusters which gave up their charges only very slowly because of the mutual shielding of an aggregate.

[16] G. Jaffé, Ann. Physik **25**, 257 (1908).
[17] F. L. Mohler and L. S. Taylor, J. Research NBS **13**, 659 (1934) RP733.
[18] J. B. Whitehead and R. H. Marvin, Trans. Am. Inst. Elec. Engrs. **49**, 649 (1930); **52**, 667 (1933).
[19] J. B. Whitehead and S. H. Shevky, Trans. Am. Inst. Elec. Engrs. **54**, 603 (1935).

As seen below, we have used his general ideas to explain the various phenomena encountered here, although for the present we will not

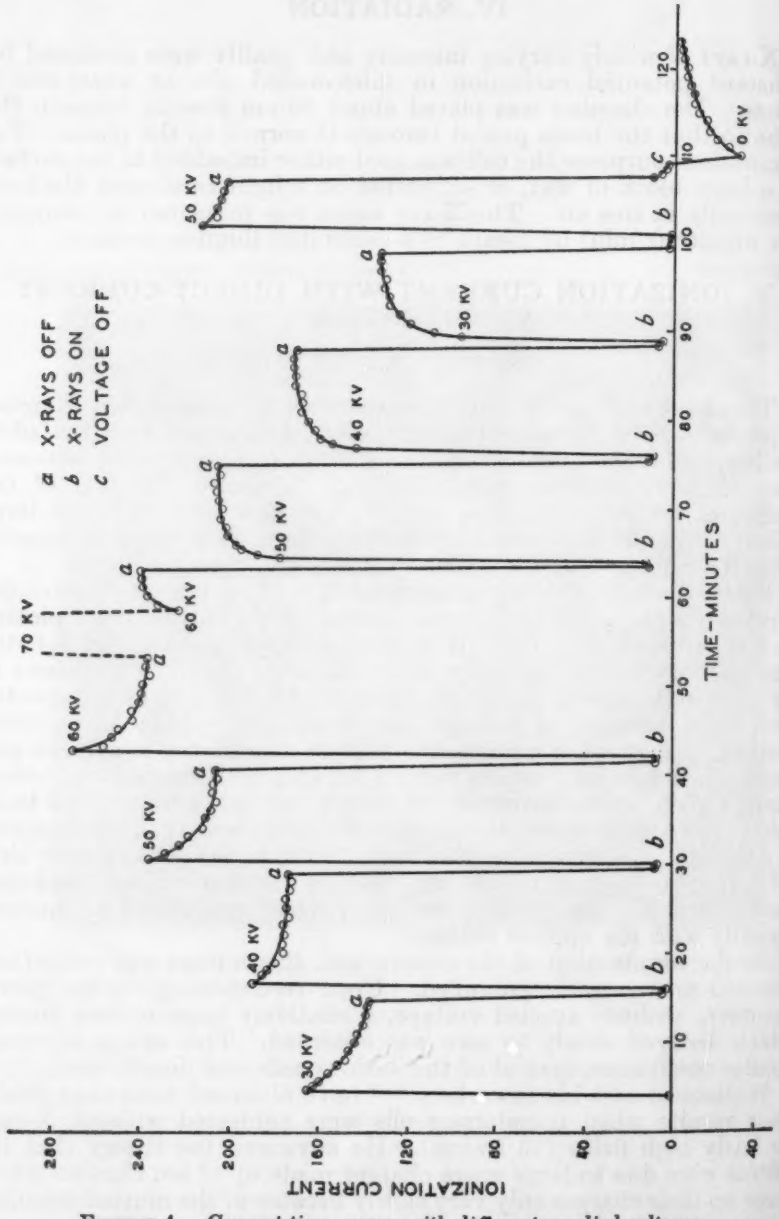

FIGURE 4.—*Current-time curves with different applied voltages.*

postulate either a space charge or other mechanism such as a polarized layer or barrier sheath at the electrodes.

In support of Whitehead's view we may outline very briefly some simple qualitative experiments with a cell filled with CS_2 and connected as shown in figure 5.

A. With the X-rays off, a negative voltage (–V) was applied to the plate *a*. The negative current to *b* had initially a high value i_1, then fell off, as indicated likewise in figure 4, to an essentially steady value in approximately 10 min. Such action may be explained by: (a) the building up of a negative space charge in the liquid or a negative sheath of bound charges at electrode *a;* (b) the initial removal of a large fraction of the ions, which have accumulated in the field-free liquid before the voltage is applied, followed by a much smaller current representative of the rate of production of new ions.

B. After reaching a steady state, the voltage was removed and the cell electrodes momentarily earthed to remove any accumulated charge. On reconnecting the galvanometer, there was a small positive current, $i_2 < i_1$, to *a*, which decayed to zero in a few minutes. Assuming a space charge in the chamber, removal of the voltage essentially reverses the field within the cell and causes a current in the external circuit opposite in direction. If X-rays are applied to the chamber immediately after the removal of voltage, the positive current flow has a much higher initial value than the small one just mentioned, and appears to reach a steady dark-current state more quickly. Approximately the same quantity of electricity appears to flow in both cases—that is, the area under the time-current curves would be the same. The evidence of space charge is also checked by the charging (up to several hundred volts) of an electrometer connected to the cell after removing the voltage.

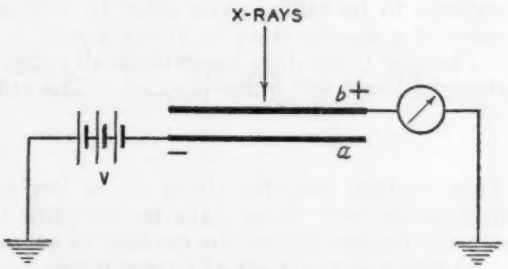

FIGURE 5.—*Simple circuit arrangement of cell.*

C. The unconnected chamber was first exposed to X-rays for some minutes, after which the X-rays were removed and voltage applied. In this case, a large initial negative current, $i_3 \gg i_1$, was soon followed by the usual decrease to a lower steady dark-current value. This was produced by an accumulation of ions in the field-free cell being cleared out to merely spontaneous-conduction conditions. The slow decay, rather than nearly instantaneous drop in current, could be ascribed to the building up of a space charge by the moving ions.

D. With X-rays on continuously, and the voltage changed in steps, the curves in figure 4 were obtained. They may be explained in the same way.

E. When using a grid-type chamber immersed in a large volume of liquid, the time required for the current to reach a steady state under any of the conditions noted, is about twice that required in the case of plate electrodes immersed in the minimum amount of liquid; but the end values of the current are the same. This might possibly be interpreted as indicating a volume distribution of space charge rather than a surface distribution, since it would be expected

that the latter would be built up, independently of the amount of liquid which circulated between the plates.

2. FORM OF CURRENT-TIME CURVES

It is obvious from the preceding that "conductivity" has little significance without specifying the time lapsed between the application of voltage and measurement of the conductivity. For the purposes of our study, it is also necessary to know the effective field within the chamber. We accordingly investigated the form of the direct-current current-time curves.

For measurements at intervals greater than a minute, a short-period galvanometer was used; for shorter intervals, a string electrometer, with a period less than 0.005 sec measured the potential drop over a resistor of about 10^9 ohms (S.S. White). Transit times past the scale divisions were observed visually and recorded on a chronograph tape; longer intervals were timed with a split-second stop watch.

Figure 6 shows two current-time curves obtained with a 1-mm grid ionization chamber exposed to X-rays and having applied voltages of 20 kv and 40 kv/cm, respectively. The 20-kilovolt curve appears to be falling even after 15 min, while the 40-kilovolt curve reached a steady state in about 9 min.

Plotting these data logarithmically (fig. 7), it is seen that they are straight lines, not quite parallel. The current for 20 kv is given by

$$i=43t^{-0.077}.$$

This relation held for times T_0 as low as 0.5 sec. It is obviously impossible from these data to compute the current for $T_0=0$; and equally impossible for the current to become infinite at $T_0=0$.

Figure 8 shows a set of curves made under the same general conditions as those in figure 4—voltage increasing and decreasing by steps. The curve (circles) for increasing voltage are roughly parallel; likewise the curves for decreasing voltage (dots) are also roughly parallel. They appear, however, to be made up of two distinct parts, and also have a slope opposite in direction to that of the other curves. The point of intersection of the two curves for the same applied voltage may be taken as the logarithm of the time required to reach an essentially steady state. As indicated by the broken line these times appear to decrease with increasing voltage, as noted previously in connection with figure 6.

It is interesting to remark that Wikstrom [20] has found for solid dielectrics (not exposed to X-rays) similar exponential relationships between current and time—the exponent remaining nearly constant with changes in field strength. His explanation was based on volume polarization—an explanation which would not be satisfactory for nonpolar CS_2. Moreover, Whitehead and Marvin [21] have made probe measurements, which show potential gradients that would be produced by space charge localized near the electrodes. Kerr effect measurements by Moeller [22] corroborate Whitehead's findings, except that they show an asymmetry in the fields at the positive and negative plates.

[20] A. Wikstrom, Physics **6**, 86 (1935).
[21] J. B. Whitehead and R. H. Marvin, Trans. Am. Inst. Elec. Engrs. **49**, 649 (1930).
[22] R. Moeller, Phys. Z. **30**, 20 (1929).

3. MEASUREMENTS OF THE EFFECTIVE FIELD STRENGTH

The presence of a space charge has the effect of introducing a barr er potential within the cell, thereby reducing the average field

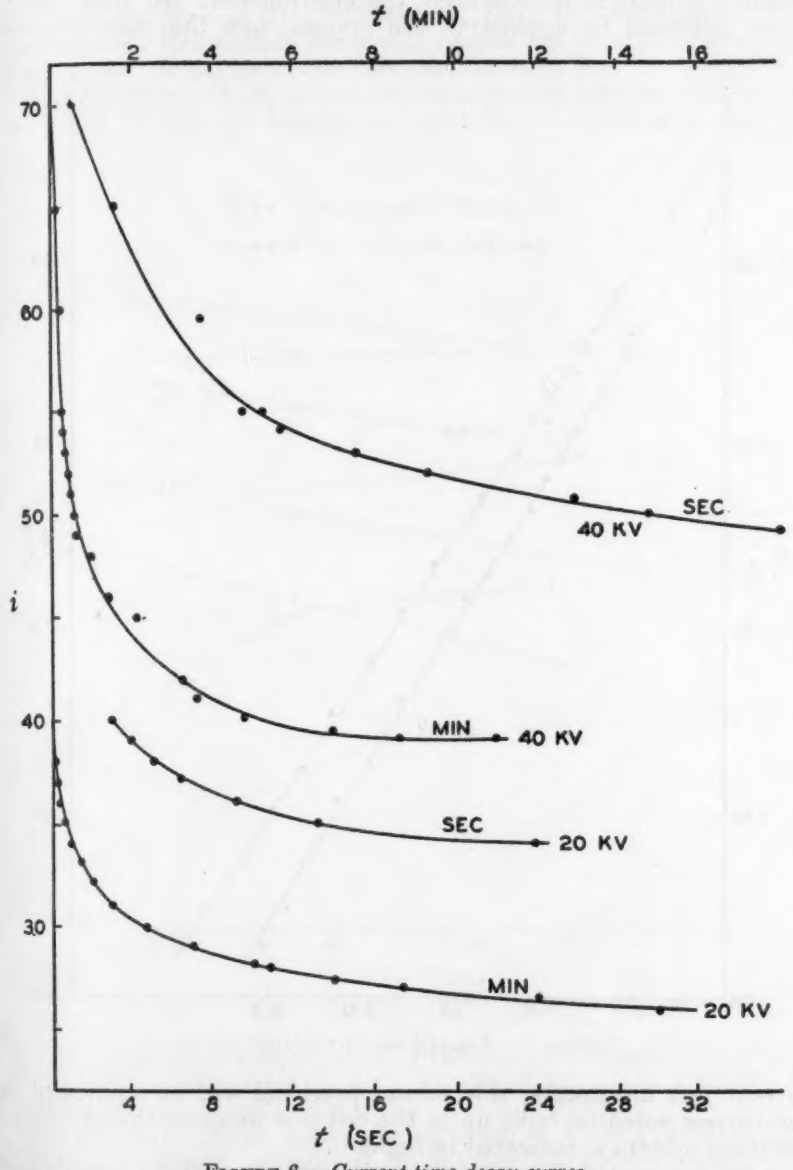

FIGURE 6.—*Current-time decay curves.*

strength to some value less than that to be expected from the applied voltage. Insofar as concerns the determination of the ionization at infinite field, it at least necessitates a longer extrapolation.

The magnitudes of the barrier potential were determined in a manner similar to Richardson's [23] method for measuring polarization. As noted above, if after an application of a potential to the cell for a certain time, it is removed and the plate earthed momentarily, a negative current is indicated by the electrometer. If, then, a different potential be applied to the system such that the negative

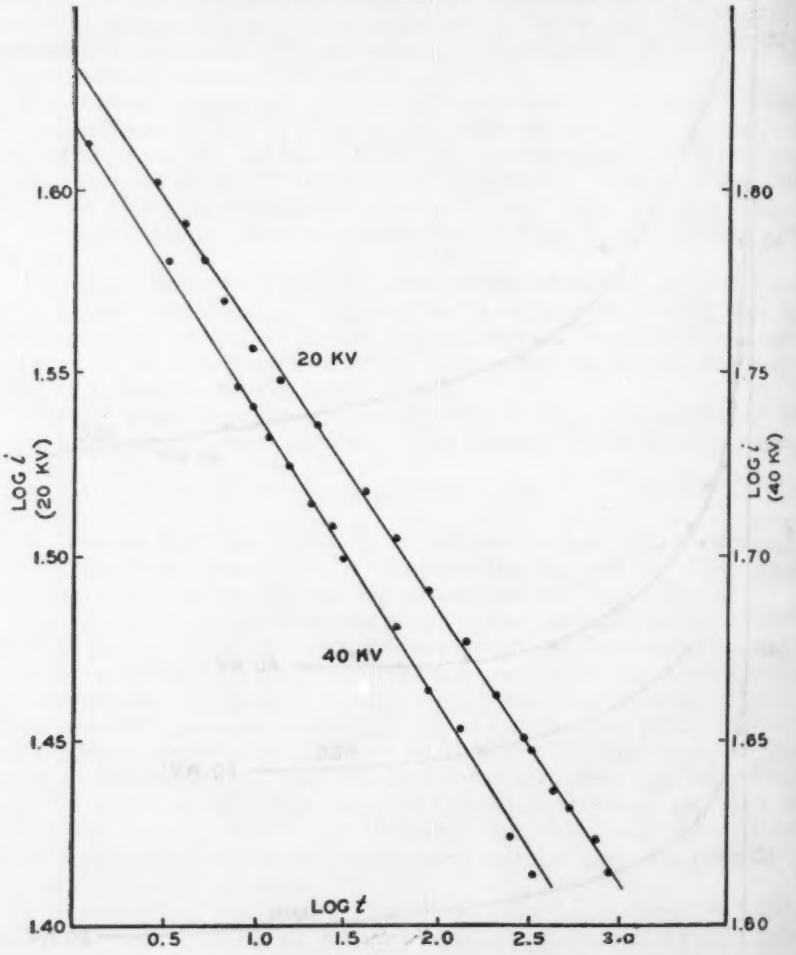

FIGURE 7.—*Logarithmic current-time curves.*

current just disappears, this second potential will be equivalent to the barrier potential built up in the cell due to space charge.[24] The electrical system is indicated in figure 9.

A hand-operated rotary switch connects the cell for any desired period with a source of potential $+V_1$. By swinging the arm S, as indicated by the arrow, the cell is momentarily grounded by segment G, and then connected to an adjustable potential, $+V_2$. Dur-

[23] S. W. Richardson, Proc. Roy. Soc. [A] **92**, 101 (1915).
[24] L. S. Taylor and F. L. Mohler, Phys. Rev. **47**, 805 (1935).

ing this time the electrometer is grounded, but at the end of the stroke the arm S depresses an insulating plunger P, which operates a multiple electrometer key, first, ungrounding the cell by opening a; second, connecting the cell to the electrometer system by closing b; and third, ungrounding the electrometer by opening c. This operation is repeated, each time adjusting V_2, until the electrometer shows no impulse. Reasonably consistent results are obtainable in spite of small speed variations in the hand operation of S.

Figure 10, graph A, shows the relationship between the applied potential V_1 and the barrier potential V_2, in which it is seen that

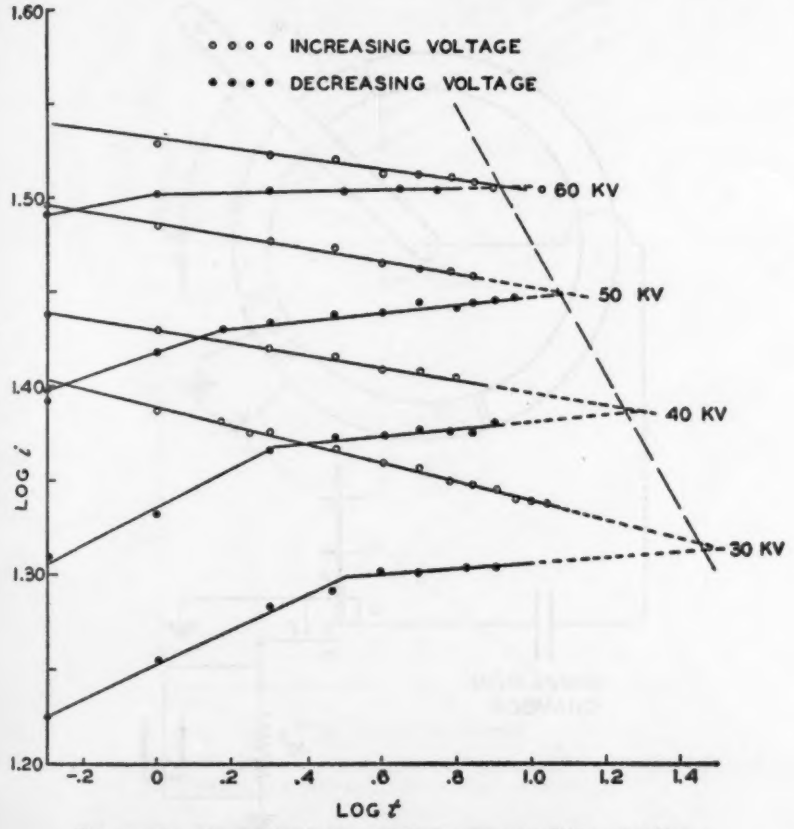

FIGURE 8.—*Logarithmic current-time curves at different voltages.*

V_2 is strictly proportioned to V_1 over the whole range of potentials used. Curve 1 was taken with X-rays of moderate intensity and curve 2 with no X-rays.

Figure 10, graph B, shows the variation of V_2 as a function of the radiation intensity (controlled by varying the tube current). It is seen here that the largest barrier potential is built up without exposure to radiation and that its value decreases steadily with increase in radiation intensity. This is perhaps contrary to expectations that a higher degree of ionization would produce a greater space charge. It is probably explained, however, by the fact that the increased

conductivity of the liquid permits a more rapid dissipation of space charge or ion clusters, which more than offsets the gain in charge due to a greater ionization density throughout the liquid.

4. DIRECT-CURRENT "CLEAN-UP" OF LIQUIDS

With newly purified liquids there is, in addition to the decrease in conductivity due to space charge, a very much slower decrease due to electrical clean-up. In fact, such a clean-up has been applied by Nikuradse[25] as a phase of his purification process in the preparation

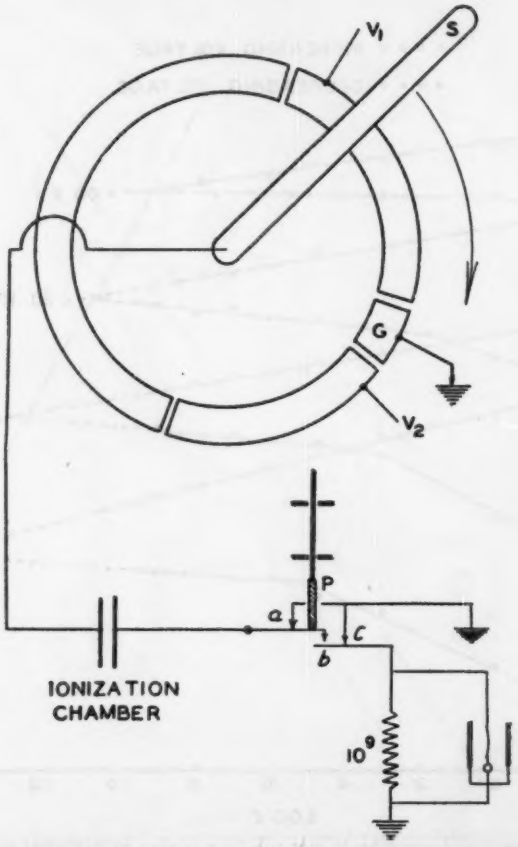

FIGURE 9.—*Switching arrangement used in determination of the barrier potential.*

of oils for power-factor measurements. Depending upon the type of cell and volume of liquid, electrical clean-up in our cells continued for 2 to 24 hr. Once a liquid had been so cleaned it showed relatively little recovery of conductivity.

Whitehead[26] in studying the current-voltage curves of transformer oils at field strengths up to 10 kv/cm reports the attainment of a saturation current. We fail to check this result with any of the liquids studied (no transformer oils). Figure 11 shows a typical current-

[25] A. Nikuradse, Z. phys. Chem. [A] **155**, 59 (1931).
[26] J. B. Whitehead and P. H. Marvin, Trans. Am. Inst. Elec. Engrs. **49**, 649 (1930).

voltage curve for CS_2, not exposed to X-rays. It is evident that while the curve is very much flatter than for the same cell when exposed to X-rays, it still shows no evidence of saturation. This particular test was carried out with CS_2 which had been subjected to careful electrical clean-up.

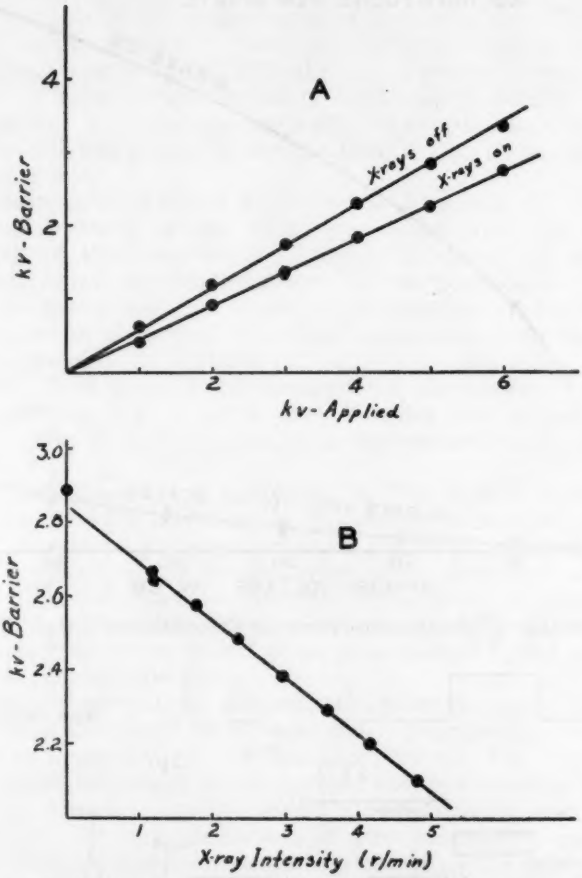

FIGURE 10.—*A, barrier potential as a function of the applied potential; B, barrier potential as a function of the radiation intensity.*

VI. SHORT-PERIOD IONIZATION-CURRENT MEASUREMENTS

1. CURRENT-MEASURING SYSTEM

To be certain that the space charge had no effect other than to effectively decrease the average field strength in the cell, direct-current measurements of the ionization were made for values of T_0 ranging as low as 0.005 sec. This gives an approach, at least, to the conditions before any space charge has been built up.

A square-wave voltage, such as indicated in figure 12, part *A*, was supplied to the potential electrode of the cell by means of a group of

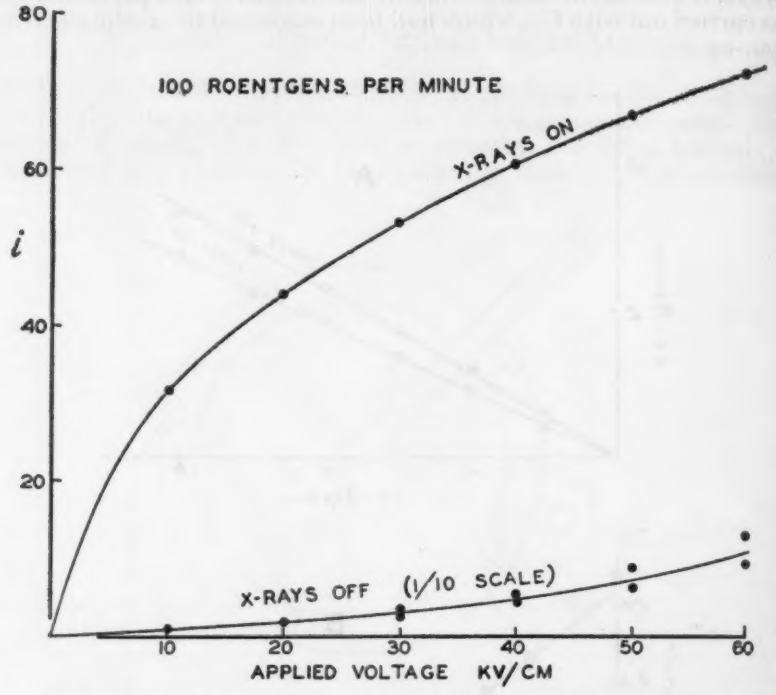

FIGURE 11.—*Current-voltage curve for* CS_2, *with and without X-rays.*

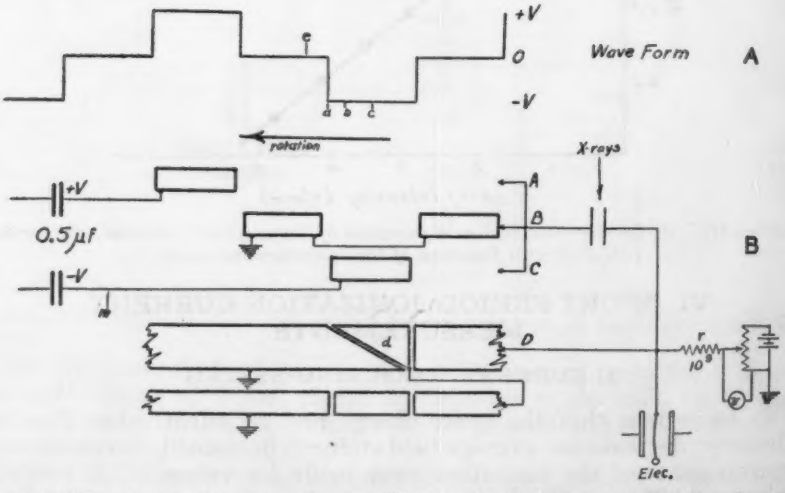

FIGURE 12.—*A, square-wave voltage applied to cell; B, Commutator system for producing square-wave voltage, and current selector.*

commutators operated on a single shaft and driven by a variable-speed direct-current motor. Part *B* of figure 12 shows the commu-

tators developed onto a plane in order to indicate the proper phase relations. Brushes A, B, and C are connected alternately to $+V$, ground, and $-V$ through the commutators. The direct-current voltage is supplied from a kenotron rectifier having a capacitance of 0.5 μf, this capacitance being so large in comparison with the remainder of the system that the division of voltage introduced no measurable drop in the capacitance of the rectifier. While a small drop is of no importance in itself, its recovery would induce a charge in the electrometer system. The absence of such recovery was tested by means of a moderate-frequency high-voltage string voltmeter [27] attached at m. At the same time a separate capacitance several times that of the cell was placed in the position of the cell in order to exaggerate any effect.

The electrometer system is connected to brush D, which keeps the system earthed, except when in contact with the segment d. The length of this ungrounded interval is varied by adjusting D at different points across the rotor. Phase position is adjusted by rotating the brush holders. The fifth commutator is for the purpose of keeping sector d earthed while not connected to the electrometer; this is to prevent its picking up any stray charges. By suitable adjustment it is possible to connect the electrometer to the cell at any point, such as b, at a time T_0 after the voltage reaches a maximum value at a, and to maintain the connection for any interval such as b–c.

A string electrometer is connected to the system as shown, with a potentiometer for adjusting a balancing voltage applied across resistance r, which is of the order of 10^9 ohms. Resistance r also serves as a shunt to the electrometer which thus acts as a current indicator. Flexible shielded rubber cables lead to the cell, commutator, etc. The system was calibrated at the beginning and end of each run, but over a period of 18 months was found to vary only about 2 percent in sensitivity.

In making observations, the potentiometer voltage v was adjusted until flicker of the electrometer essentially disappeared; the ionization current was given by v/r. When the interval, b–c, was made too long, complete balancing of the current was not possible because the building up of space charge caused an appreciable lowering of the conductivity. In such cases one of two procedures was followed. First, the balance condition would be taken as the point where the electrometer impulse just ceased to occur in the over-balance direction. After the first few trials this point could be repeated with fair accuracy. Secondly, a neon lamp, used for illuminating the electrometer scale, was synchronized with the commutator drive shaft so as to cease glowing at a very short interval after b, thereby making it impossible to see the fiber except at the time of the maximum ionization current. This method simplified the balancing, but caused eye fatigue; consequently, the first method was used most of the time.

The interval T_0 was set by varying either the phase position of d or the frequency of the applied voltage. This latter was adjustable within a range 0.01 to 30 rps and was controlled by means of a generator tachometer on the main shaft.

[27] L. S. Taylor, BS J. Research 5, 609 (1930) RP217.

To test for the absence of accumulated space charge, the selectors were adjusted so as to give a current reading, should such exist, at some point such as *e*. In no case was a measurable current observed.

2. CURRENT-TIME CURVES

With fixed values of V the net ionization current was measured as a function of T_0, which was varied by means of the frequency of the voltage alternations—the "dark current" being subtracted from the total in each case. Figure 13 shows a typical curve taken with a high value of V and with a fairly intense beam of radiation (about 75 roentgens per minute). The current scale is arbitrary.

The position of the break, *b*, appears to depend on both the applied voltage and the intensity of the radiation, qualitative measurements indicating that T_b increases with ionization density and decreases

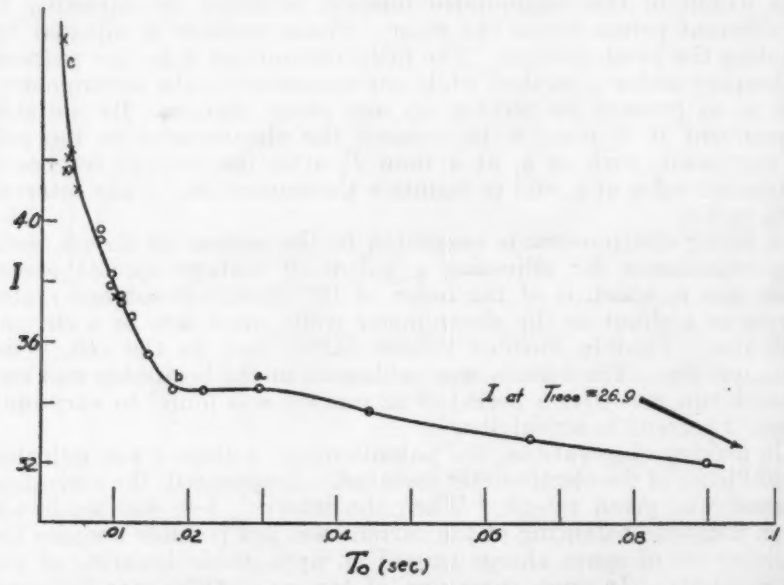

FIGURE 13.—*Current-time curves for interrupted voltage.*

with increase in V. It may also be noted that the value of I in the region *ab* is roughly what would be expected in a liquid free of space charge, on the basis of independent measurements of the barrier potential.

Throughout these experiments the liquids were exposed to X-rays almost continuously, as a consequence of which the ion density without applied voltage would be very large. Thus, when the voltage is first applied to the chamber at $T_0=0$, there is this large number of ions which must be swept out before the current indication gives a measure of the rate of production of new ions. The passage of these accumulated ions would account for the portion of the curve *bc*.

However, at the fields used here (40 to 50 kv/cm) the velocity of CS_2 ions is of the order of 300 cm/s[28] so that the expected time neces-

[28] Van der Bijl, Ann. Physik **39**, 170 (1912).

sary to clear the cell would be the order of 0.003 sec, whereas in all of our curves the point b is in the neighborhood of 0.02 sec. A number of possible explanations present themselves—perhaps the simplest of which is the effect of space charge. With the application of potential to this uniformly ionized liquid, there takes place a segregation of positive and negative ions, which, in turn, establishes a barrier potential and intensifies the very conditions we are studying. With the application of an electric field, this high ion density cannot be maintained and hence the discharge current is of a short duration. Then, at point b the effect due to newly produced ions becomes dominant, and extends over longer periods of time. It may well be that the two effects combine to make up the portions of the curve below b, although judging by the very rapid decrease in I between c and b, its effect probably soon becomes negligible.

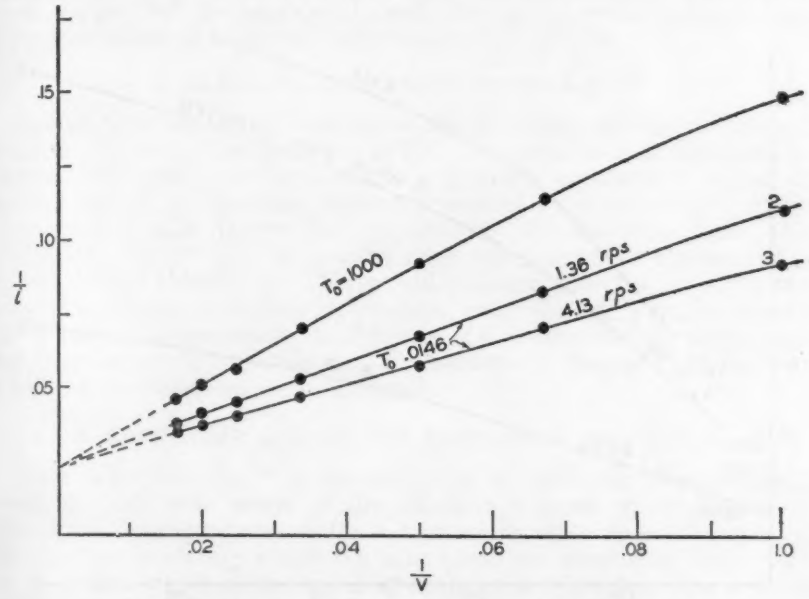

FIGURE 14.—*Inverse current-voltage curves—T_0 varied.*

An alternative explanation for the shape of this curve might depend upon the existence of heavy-ion aggregates in the field-free liquid. These, having a much lower mobility, would be cleared more slowly from the cell. The position of the break b would give to these ion aggregates a velocity of about 30 cm/s which is a reasonable value, corresponding to a mobility of the order of 6×10^{-4} cm/s/v/cm. The portions cb appear to be roughly of the form $I=kt^{-2}$, although the points are somewhat scattered.

3. INVERSE CURRENT-VOLTAGE CURVES

Figure 14 gives a group of curves showing the relationship between reciprocal current (arbitrary units) and reciprocal voltage for the same X-ray intensity but under different conditions of measurement. Curve 1 is for direct-current conditions ($T_0=10$ min); curve 2, for a

square-wave voltage of 1.36 cycles/s, and curve 3 for 4.13 cycles/s; the timing selector was set for $T_0=0.0146$ sec in both cases. It is clearly evident that all curves pass through the same point at $1/V=0$.

The difference in slope between the different curves is associated with the barrier potential or space charge, and it is probable that if actual average field strengths were used for abscissas in place of $1/V$, all the curves would coincide. This may be seen from Jaffé's equation, which is of the form $1/I_x=C_1/X+C_2$, so that if C_2 is constant and $1/I_\infty$ is the same, then the slope C_1 must vary directly with $1/X$.

Thus, comparing curve 1 (full space charge) with curve 3 (no space charge) we find a slope ratio of 1:2.4, from which we may deduce, on the basis of the abscissas for curve 3 being effective field strength, that the effective field for direct-current potentials is in this case only about 42 percent of the applied field, and which is of the right order. This may be a somewhat risky conclusion since it may not

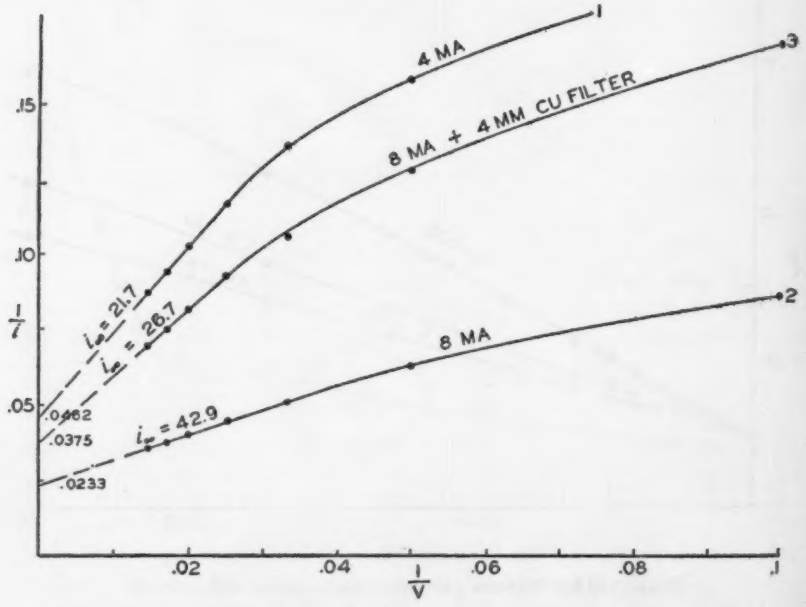

FIGURE 15.—*Inverse current-voltage curves—X-ray intensity varied.*

be definitely known what value of T_0 should be used for zero space charge. A further complication is introduced when we note that curves 2 and 3 differ markedly in slope in spite of both having the same value of T_0, but differing in frequency. When T_0 is varied while holding the frequency constant, the slopes of the curves vary in accordance with the expectations based on figure 8, all curves again passing through the same point at $1/V=0$.

4. X-RAY-INTENSITY MEASUREMENTS

The variation of I_∞ with the intensity of the radiation is shown in figure 15, curves 1 and 2 being obtained at 160 kv (constant) with 4 and 8 ma, respectively. The values of I_∞ obtained by extrapolation are 21.7 and 42.9, being within experimental limits in the ratio of 1:2.

The proportionality of I_∞ to intensity has been found to hold within a range of at least 20:1 for a given quality of radiation.

When the quality of the radiation is changed at the same time as the intensity, the proportionality of I_∞ and intensity as measured by air ionization no longer holds. Curve 3, for 8-milliampere and 0.4-millimeter copper filtration, gives a value for $I_\infty = 26.7$, making a ratio of 2.13 with the value of I_∞ at no filtration. This compares with a similar ratio of 1.61 obtained by air-ionization measurements with a calibrated thimble ionization chamber.

It may be pointed out that when comparing X-ray intensities of a given quality by means of a liquid ionization chamber, single measurements made at a given chamber potential may be used, provided they fall on the straight portions of the curves. Potentials corresponding to the curved portion of the plots can only rarely be used in intensity comparison. With direct current applied fields in excess of 25 kv/cm must, in general, be used, while with the square-wave voltage, field strengths as low as 10 kv/cm may sometimes be used.

5. ALTERNATING-CURRENT CLEAN-UP

It may be noted, that contrary to the fact that liquids are subject to direct-current clean-up, there is little or no evidence of alternating-current clean-up. As the liquid in a chamber ages over a period of several weeks, the leakage current produced by a pulsating voltage may grow steadily larger, but not always. On the other hand, the ionization current due to X-rays does not change to a measurable extent during this time. This would indicate that the liquid is not subject to an effective chemical change, other than to a small amount of electrolytic dissociation; in the case of CS_2 some sulphur separates out from exposure to sunlight. The important fact is that the net effect due to radiation is not changed.

6. EFFECTIVE VOLUME OF IONIZATION CHAMBER

Since it is desired to use the grid type of electrode in subsequent work, a study was made of the effective volume of an ionization chamber having grid electrodes. Aluminum wires about 0.1 mm in diameter were strung about 0.9 mm apart on aluminum rings (see fig. 3) two of which were placed on both faces of a fused-quartz plate about 70 mm in diameter and having a hole about 1 cm in diameter at the center. Several such plates having thicknesses (d) of 0.5, 1.0, 1.5, 2.0, and 2.5 mm were used. The electrodes were so shielded as to prevent any ionization reaching the measuring electrode except from the volume occupied by the hole in the quartz plate.

Reciprocal plots of the ionization current were obtained for different volumes, under the same X-ray conditions, from which saturation currents, I_∞ given in table 1, were obtained by extrapolation.

TABLE 1

Cell thickness (d)	$1/I_\infty$	I_∞	I_∞/d
mm			
0.5	0.405	2.47	4.94
1.0	.205	4.88	4.88
1.5	.138	7.24	4.83
2.0	.102	9.80	4.90

I_∞/d gives a measure of the ionization per unit volume at different cell thicknesses, and it is seen that the maximum deviation from the mean is only slightly over 1 percent, which is probably less than the experimental error. Comparisons between the ionization per unit volume measured with grids and with thin (0.2 mm) aluminum plates were in fair agreement—the greatest source of uncertainty being the absorption correction necessary for the plates.

7. IONIZATION WITHOUT X-RAYS

As an explanation of the residual conductivity of such liquids as here used, it has been variously suggested as due to the ionization produced by cosmic radiation.[29] [30]

However, the conductivity of the purest liquids we have been able to obtain (tetralin) has been much too large to be accounted for on such a basis. For example, the X-ray intensity used for the 8-milliampere curves in figure 15 was of the order of 100 r/m, and gave a value $I_\infty=42.5$. At the same time, the dark current or residual conductivity was 0.5 at a field strength of 60 kv/cm, which would correspond to about 1.1 r/min. This, compared with a cosmic-ray intensity of the order of 10^{-5} r/min makes it obvious that cosmic rays cannot have an appreciable effect upon the residual conductivity. It may be possible that a portion of the residual conductivity occurs through the body of the quartz, which has about 10 times the area between plates as the CS_2. Even assuming equal conductivities for quartz and CS_2 (which is contrary to experience) there is a discrepancy of 10^4 between the measured and calculated cosmic-ray ionization.

8. UNIPOLAR CONDUCTIVITY

In a short abstract of this work [31] mention was made of a unipolar conductivity in CS_2. Careful subsequent measurements failed to verify this effect for either steady or fluctuating voltages—our earlier measurements evidently having been subject to some undetected error. On the other hand, several observers have reported a unipolar conductivity.[32] It is probable that their findings are influenced by asymmetrical field conditions introduced through the use of cylindrical electrodes,[33] [34] or point to plate electrodes.

WASHINGTON, July 2, 1936.

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP928

Part of Journal of Research of the National Bureau of Standards, Volume 17, October 1936

OXIDATION OF WOOL: ALKALI-SOLUBILITY TEST FOR DETERMINING THE EXTENT OF OXIDATION [1]

By Milton Harris and Arthur L. Smith [2]

ABSTRACT

Oxidizing agents attack the disulfide groups of the cystine in wool and increase the solubility of the wool in alkaline solutions. The determination of the alkali-solubility may be used as a measure of the extent to which the wool is oxidized. The method is applicable as a control in practical processes, such as bleaching and chlorination, and offers a measure of the extent to which wool is degraded by photochemical reactions. Data are presented which indicate a relationship between the chemical and physical degradation of wool fibers.

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I. INTRODUCTION

In practical processing, wool is often exposed to conditions in which it may become partially oxidized. Under extreme conditions, such as may be encountered during severe bleaching or chlorination, the wool is oxidized to such an extent that the damage is readily detectable by visual examination or by ordinary physical testing methods. In well-controlled processes, however, the amount of oxidation is barely or not at all measurable by ordinary testing methods. The incipient damage which may be produced by mild oxidation is usually developed and accentuated during subsequent processing. It is apparent, therefore, that analytical methods for determining the extent of oxidation of wool are of importance for effective control during its processing.

In a series of studies relating to the oxidation of wool and to the effect of alkalies on untreated and on oxidized wool [1, 2, 3, 4],[3] it was shown that the main point of attack by both oxidizing and alkaline reagents was the disulfide group of the cystine in wool. It was also

[1] This is the fourth paper of a series of studies relating to the oxidation of wool.

[2] Research associates at the National Bureau of Standards, representing the American Association of Textile Chemists and Colorists.

[3] The numbers in brackets here and elsewhere in the text relate to the numbered references at the end of this paper.

shown that the oxidized wool is more susceptible to alkaline treatment than untreated wool, and that the extent to which the wool is oxidized bears a functional relationship to the decrease in the cystine content and to the increase in the alkali-solubility. Although determinations of either the cystine content or the alkali-solubility are measures of the extent of oxidation of wool, the former is not practical since it requires equipment, technique, and time which are not ordinarily available in the average textile-mill laboratory. On the other hand, the latter method is comparatively rapid and simple, and, in most instances, appears to be more sensitive.

The present paper deals with the application of the alkali-solubility test to a number of practical processes in which wool is subjected to oxidation reactions. Comparative data obtained from corresponding cystine analyses are also presented.

II. METHODS

Alkali-solubility was determined by treating the wool with a 0.1 *N* solution of sodium hydroxide at 65° C for 1 hour, the ratio of wool to solution being approximately 1:100, by weight. The wool was recovered on a Büchner funnel, washed with about 2 liters of water, dried to constant weight at 105° C, and the loss in weight determined. Samples of wool which had been severely oxidized became gelatinous during the alkali treatment. These samples were partially dried in an oven at about 50° C for 1 hour and then dried at 105° C. The cystine content was determined by the Sullivan method [5]. Data showing the reproducibilities which may be expected by both methods are given in table 1.

TABLE 1.—*Results of six analyses of untreated wool yarn to show reproducibility*

The values are based on the oven-dry weight of the wool.

Alkali-solubility	Cystine content
%	%
12.5	11.5
12.9	11.4
12.9	11.3
11.6	12.0
13.1	11.3
12.5	11.5
Average 12.6	11.5
Average deviation from the mean 0.4	0.2

III. APPLICATIONS OF THE ALKALI-SOLUBILITY TEST

1. HYDROGEN PEROXIDE BLEACHING

In a previous paper [2] on the effect of hydrogen peroxide on wool, data were presented showing the effects of varying the concentration, temperature, and pH of the hydrogen peroxide solutions and the duration of the treatment. Data taken from that paper on the effect of varying the temperature of the bleach bath are presented in table 2 as a typical example of the use of the alkali-solubility test for studying and controlling the bleaching process.

TABLE 2.—*Effect on wool of 2-volume (0.6%) solutions of hydrogen peroxide at various temperatures from 23 to 80° C, for 3 hours; and the alkali-solubility of the treated wool*

Temperature of H_2O_2 solution	Alkali-solubility	Cystine content after treatment with H_2O_2
°C	%	%
23	9.7	11.2
35	13.6	11.3
50	19.4	10.8
65	31.6	9.8
80	100.0	7.4

The use of the method as a control for commercial bleaching operations was also investigated. The effects of successive commercial bleaching treatments on wool cloth are recorded in table 3. The values for the swelling, shown in the last column of table 3, were obtained by Von Bergen's method [5].[4] The results obtained by all of the methods are in good agreement, but the swelling method, like that for cystine, requires technique and equipment which are not usually available.

TABLE 3.—*Effect of commercial bleaching on the alkali-solubility, cystine content, and swelling in alkali of wool cloth*

The wool was bleached in hydrogen peroxide at pH 9.8 and at a temperature of 120° F. The concentration of the hydrogen peroxide and the duration of the treatment are indicated in the table. After each bleaching treatment, the wool was washed, immersed for 20 minutes in a bath containing 1.2 percent of sulphuric acid and 0.25 percent of sulphur dioxide, and washed in running water for 15 minutes]

Sample	Treatment	Alkali-solubility	Cystine content	Swelling
		Percent	*Percent*	*Percent*
1	None	11.1	12.8	12.4
2	Bleached with 2.71-vol. H_2O_2 for 1½ hr	17.2	11.7	14.7
3	Sample 2 bleached with 2.62-vol. H_2O_2 for 1½ hr	20.3	11.3	18.6
4	Sample 3 bleached with 1.70-vol. H_2O_2 for 1 hr	31.4	10.8	21.2

The values obtained for the alkali-solubility of a given wool sample will vary not only with the extent of oxidation but also with the construction of the material being tested; that is, the amount of surface exposed. For example, a given sample of wool will lose more weight when it is in the form of yarn than when it is in the form of a closely woven fabric. Consequently, in using the alkali-solubility test as a control in practical bleaching, the tolerances chosen will depend on the type of material being processed as well as on the uses to which it will ultimately be subjected.

2. CHLORINATION AND BROMINATION

The use of chlorine and bromine for the production of unshrinkable wool textiles has recently received much attention. In addition, the chlorination process is frequently used to improve the luster of wool. The great affinity of wool for these halogens and the ease with which

[4] These determinations were made by Dr. Von Bergen, chief chemist, Forstmann Woolen Co., Passaic, N. J.

the fiber is damaged by them are the chief reasons for their limited use. The evaluation and minimizing of the damage are two of the important problems connected with the successful use of the processes. Since the degradation of wool by halogens appears to be brought about by oxidation reactions, the alkali-solubility test was used to study the effects of the chlorination and bromination processes.

Samples of wool yarn, each weighing approximately 4 g, were treated for 20 minutes at room temperature with 160-milliliter portions of sodium hypochlorite and hypochlorous acid solutions, varying in concentration from 1 to 8 percent of chlorine based on the weight of wool. The effects of the treatments are recorded in table 4.

TABLE 4.—*Effect on wool yarn of sodium hypochlorite and hypochlorous acid solutions of various concentrations at room temperature for 20 minutes*

Treatment	Concentration [1] of chlorine	Change in wt during chlorination [2]	Alkali-solubility	Cystine content
	%	%	%	%
None	0	0.0	11.0	11.6
NaOCl	1	−.1	15.3	9.5
Do	2	−.3	15.2	9.2
Do	3	−1.1	29.7	9.4
Do	4	−2.4	28.4	9.5
Do	6	−5.2	26.0	9.5
Do	8	−8.0	25.3	9.2
HOCl	1	+2.2	24.0	9.3
Do	2	+2.6	30.1	9.0
Do	3	+0.5	34.9	8.9
Do	4	−6.3	36.6	7.9
Do	6	−7.9	37.9	6.7
Do	8	−13.1	43.5	6.8

[1] Based on the weight of wool. [2] Plus sign indicates gain in weight; minus sign, loss in weight.

With the exception of those samples treated with sodium hypochlorite solutions of concentrations higher than 4 percent, the alkali-solubility increased and the cystine content decreased with increasing concentrations of chlorine. The apparent discrepancies may be attributed to the fact that the more concentrated solutions of sodium hypochlorite probably dissolve a portion of the wool that would ordinarily be removed by the subsequent alkali treatment.

It has long been known that the chlorination process tends to reduce the wearing qualities of woolen fabrics. Various investigators have attempted to estimate wearing quality of chlorinated wool by relating it to tensile strength, extensibility, the presence or absence of scales, the solubility of the wool in acids and alkalies, and the altered affinity of the wool for dyestuffs. While chlorination undoubtedly influences these properties, a definite relationship between them and wearing qualities has not previously been demonstrated.

From the standpoint of physical stability, the disulfide group constitutes what is probably the most important connecting link in the wool molecule. Since it has been shown that chloride attacks the disulfide group and increases the solubility of wool in alkalies, it seemed desirable to relate results of the alkali-solubility test to those obtained from actual wear tests.

Samples of carpet wools [5] which had been treated with various con-

[5] The wool used for these experiments and the wear tests on the carpets were furnished by G. E. Hopkins, technical director of the Bigelow-Sanford Carpet Co., Inc., Thompsonville, Conn.

centrations of sodium hypochlorite solutions for the purpose of producing a desired luster were analyzed for alkali-solubility and for cystine content. Wear tests on similarly treated carpets were made on a carpet wear-testing machine [6]. The numerical data are given in table 5 and shown graphically in figure 1. The results not only demonstrate further applications of the alkali-solubility test, but also indicate a definite relationship between the physical and chemical degradation of the wool fiber.

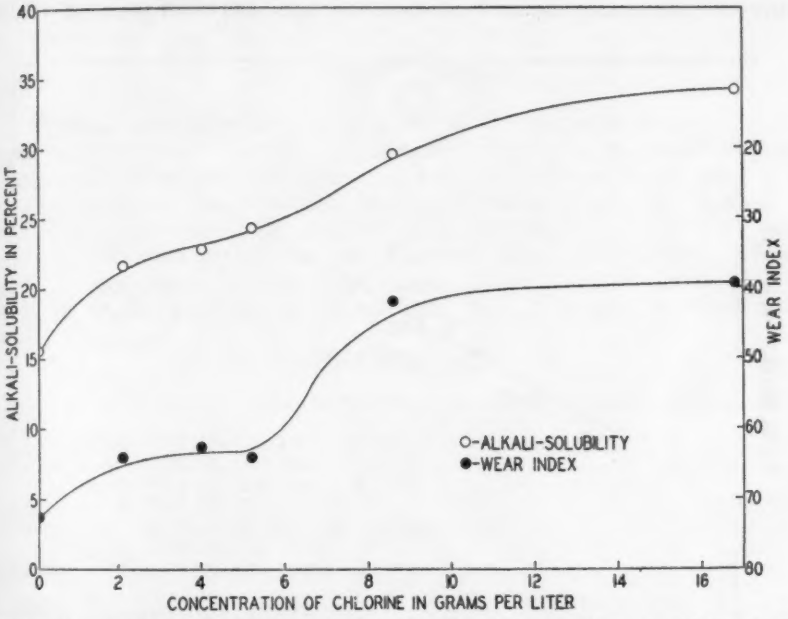

FIGURE 1.—*Effect of treating wool with different concentrations of sodium hypochlorite solution at 105° F for 1 hour on its alkali-solubility and on the wear index of carpets made from the wool.*

TABLE 5.—*Effect of different concentrations of sodium hypochlorite solutions at 105° F for 1 hour on carpet wool*

[The ratio of wool to solution was 1:20, by weight.]

Available chlorine	Wear index [1]	Alkali-solubility	Cystine content
g/liter		%	%
0	72.5	15.6	9.8
2.1	64.1	21.6	8.9
4.0	62.7	22.8	8.4
5.2	64.1	24.3	8.2
8.6	41.9	29.6	8.0
16.8	39.4	34.1	7.4

[1] The wear index of the carpet is the number of thousands of revolutions of the turntable required to wear the pile of a carpet down to one-fourth of its original pile thickness.

3. EFFECT OF LIGHT ON WOOL

The results of numerous investigations have shown that the breaking strength, milling properties, affinity for dyestuffs, and sulfur and

nitrogen contents of wool are altered during the photochemical decomposition of the fiber. However, the determination of any one of these changes does not afford a very sensitive or convenient method for measuring the amount of degradation produced by the action of light. In a recent publication [7] relating to the photochemical decomposition of wool, it was shown that the extent to which wool is degraded during irradiation is directly proportional to the decrease in cystine content and to the increase in alkali-solubility. While subsequent work has indicated that the primary action of light on wool may not necessarily be an oxidation reaction, the chief point of attack

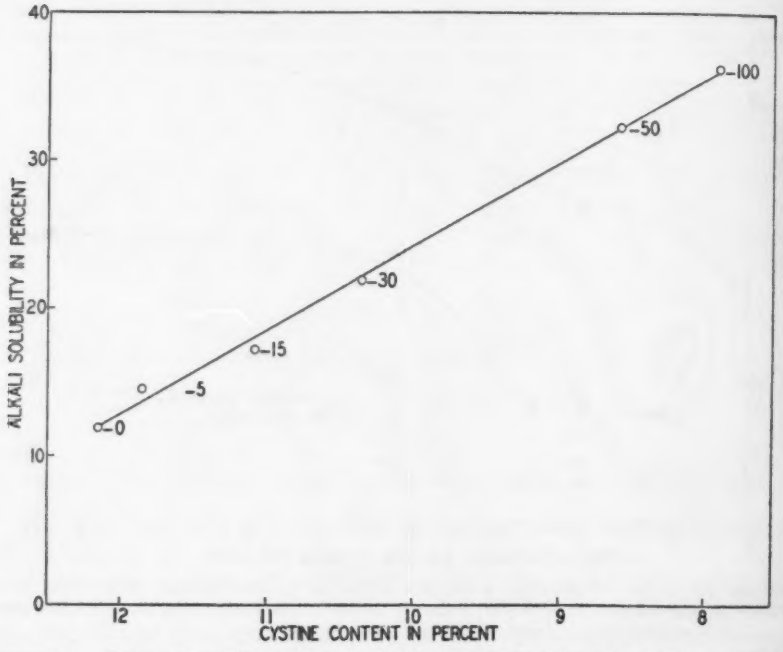

FIGURE 2.—*Effect on cystine content and the alkali-solubility of wool of exposure to the radiation of a glass-enclosed carbon arc.*

The figures on the curve represent the duration of exposure, in hours.

is still the disulfide group of the cystine in the wool, and the alkali-solubility is correspondingly increased.

Samples of wool top were exposed to the radiation of a glass-enclosed carbon arc for different lengths of time from 5 to 100 hours. The effects of the exposures are shown in table 6. When the data obtained by both methods are plotted against each other as shown in figure 2, it is readily demonstrated that there is a linear relationship between the increase in the alkali-solubility and the decrease in the cystine content of the exposed samples of wool.

TABLE 6.—*Effect on wool top of exposure to the radiation from a glass-enclosed carbon arc for different lengths of time*

Exposure	Alkali-solubility	Cystine content
hr	%	%
0	11.9	12.2
5	14.5	11.9
15	17.2	11.1
30	21.9	10.4
50	32.2	8.6
100	36.2	7.9

IV. CONCLUSIONS

The alkali-solubility test as outlined in this paper is comparatively rapid and gives sufficiently reproducible results to recommend it as a method for determining the extent of oxidation of wool and as a control method in practical wool processes involving oxidative reactions. The use of the method as a control for a specific process requires the determination of limiting alkali-solubilities. These limits will depend on the type and construction of the material being processed and the use to which it will ultimately be subjected.

V. REFERENCES

[Bracketed numbers are citations corresponding to the references in brackets in the text]

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WASHINGTON, July 29, 1936.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP929

Part of Journal of Research of the National Bureau of Standards, Volume 17, October 1936

CALCULATIONS OF ELECTRICAL SURGE-GENERATOR CIRCUITS

By Arthur B. Lewis

ABSTRACT

It is pointed out that electrical surge-generator circuits are, essentially, periodically loaded lines. It is then shown that, with the aid of certain reasonable assumptions, the well-known theory dealing with such lines leads directly to expressions for the free periods and damping factors of surge-generator circuits. The resulting equations can be solved exactly in some cases and can be solved approximately in all cases. In certain cases exact expressions can be obtained for the current and voltage amplitudes.

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I. INTRODUCTION

Recent investigations into the behavior of transmission lines and associated equipment, when subjected to voltage and current surges simulating those produced by lightning disturbances, have led to the development and use of the so-called surge-voltage and surge-current generators. A surge-voltage generator consists of a number of capacitors which are charged in parallel and then, by a suitable arrangement of spark-gaps, discharged in series. Figure 1 is a schematic diagram of the circuits of a surge-generator as they function on discharge, the charging circuits being omitted to avoid confusing the figure. If all the capacitors are identical and are initially charged to the same voltage E_0, the voltage appearing across the terminals of the nth mesh will rise to a maximum value of the order of nE_0 when the gaps are discharged in succession, beginning at the left-hand end. A surge-current generator consists of a number of capacitors which

are arranged to be charged and discharged in parallel. The current in the terminal mesh of an n-section generator will be roughly n times that obtainable from a single capacitor. Figure 3 shows a schematic diagram of a surge-current generator in which, again, the charging circuit is not shown.

The methods of obtaining approximate solutions for such circuits are obvious. If one neglects the internal structure of such a circuit and considers it to consist simply of a lumped effective capacitance, inductance, and resistance, the frequency and amplitude of the fundamental component of current or voltage can be computed with a reasonable degree of accuracy. As an additional approximation one might consider the entire generator to consist of two circuits, a generator with lumped constants coupled to a load circuit. Apparently no analyses of the discharge characteristics of surge-generator circuits have been published which have gone beyond these two obvious approximations, although R. Elsner and C. S. Roys have published complete analyses of the charging characteristics of such circuits.[1] While serving fairly well to predict the frequency of the fundamental component of current or voltage, this approximation leads to erroneous results when an attempt is made to use it in the computation of critical damping resistances, as will be shown in the section on surge-current generators. In addition, such a simplification entirely neglects the presence of frequencies higher than the fundamental. It is just these higher frequencies, however, which are of particular importance in defining the wave front of such surges.

It is the purpose of this paper to point out that surge-generator circuits are essentially periodically loaded lines, and that the highly developed theory of the periodically loaded line can be applied directly to surge-generator problems. It is shown that straightforward calculations lead to expressions for the free periods and damping factors of surge-generator circuits which can be solved exactly in some cases and approximately in all cases. In certain cases exact expressions can be obtained for the current or voltage amplitudes.

II. SURGE-VOLTAGE GENERATOR

1. STATEMENT OF THE GENERAL PROBLEM

The problem of the surge-voltage generator can be stated conveniently in terms of the simplified circuit shown in figure 1. A set of $n-1$ identical capacitors of capacitance C are first charged in parallel to a common voltage E_0. By a suitable arrangement of sphere gaps, as shown, they are then discharged in series through leads having identical resistances R and inductances L. The nth mesh, of resistance R_n, inductance I_n, and capacitance C_n, contains the equipment under test as well as other measuring apparatus, and is in general different from the other $n-1$ meshes. The capacitance to ground associated with each capacitor and its two spherical terminals is supposed, for simplicity, to be concentrated as shown in figure 1 and to be of common value C_g. Different locations of this lumped

[1] P. L. Bellaschi, Trans. Am. Inst. Elec. Engrs. **51**, 936-945 (1932); **52**, 544-552 (1933); Elec. Eng. **53**, 86-94 (1934).
J. C. Dowell and C. M. Foust, Trans. Am. Inst. Elec. Engrs. **52**, 537-543 (1933).
B. L. Goodlet, J. Inst. Elec. Eng. (London), **74**, 377-396 (1934).
K. B. McEachron and J. L. Thomason, Gen. Elec. Rev. **38**, 126-131 (1935).
R. Elsner, Arch. Elektrotech. **29**, 655-682 (1935).
C. S. Roys, Engineering Bulletin Purdue University **19**, no. 3 (May 1935). Research Series no. 50.

capacitance to ground, as for example, splitting it between the two capacitor terminals, would present no essential mathematical difficulties. We neglect the internal structure of the capacitors, if any, and assume that their internal losses are sufficiently represented by a suitable increase in the lead resistance R.

All the capacitors are initially charged to the same voltage, E_0. If now the first gap is broken down by some artificial means, each of the other gaps in the circuit will break down in its turn as the voltage across it rises to its breakdown value. The problem, then, is to find the charges on the various capacitors as explicit functions of time, subject to the given initial conditions of charge and current. Let Q_s represent the charge on the sth main capacitor and q_s the charge on the sth capacitor to ground. The method of solution is to set up the equation for the summation of the voltages around each mesh in terms of the charges on the various capacitors. The q's can be eliminated in terms of the Q's. After certain transformations the resulting n second-order differential equations in the Q's lead to a trigonometric equation of degree n, the secular equation, the roots of which furnish the free periods and damping factors of the system. These roots can be obtained exactly in some cases and can be approximated in every case. The $2n$ constants necessary to satisfy the original n second-order differential equations determine the amplitudes and phase angles of the charge components. Exact expressions can be found for these constants in certain limiting cases and approximate expressions in certain others.

2. FORMAL SOLUTION OF THE GENERAL PROBLEM

Referring now to figure 1 and writing down the equations for the summation of the voltages around each mesh, the gaps now being considered conducting,

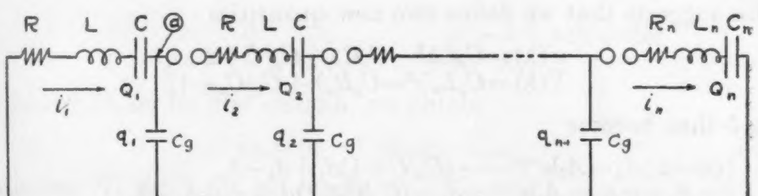

FIGURE 1.—*Schematic diagram of a surge-voltage generator.*

The charging circuits have been omitted to avoid confusing the figure.

$$\left.\begin{aligned}-Ri_1-Ldi_1/dt+Q_1/C+q_1/C_g&=0\\-q_1/C_g-Ri_2-Ldi_2/dt+Q_2/C+q_2/C_g&=0\\\cdots\cdots\cdots\cdots\cdots&\\-q_{s-1}/C-Ri_s-Ldi_s/dt+Q_s/C+q_s/C_g&=0\\\cdots\cdots\cdots\cdots\cdots&\\-q_{n-1}/C-R_ni_n-L_ndi_n/dt+Q_n/C_n&=0\end{aligned}\right\}\qquad(1)$$

Now consider the currents at a representative point, as a. By definition

$$i_s=-dQ_s/dt \qquad (2)$$

Then at point a

$$-dQ_s/dt+dq_s/dt=-dQ_{s+1}/dt$$

Integrating,

$$q_s=Q_s-Q_{s+1}+h_s \text{ (constant)} \tag{3}$$

At $t=0$,

$$\begin{aligned} q_s&=q_{s,0}\\ Q_s&=Q_{s,0}\\ Q_{s+1}&=Q_{s+1,0} \end{aligned}$$

Therefore,

$$h_s=q_{s,0}-Q_{s,0}+Q_{s+1,0} \tag{4}$$

Substituting eq 2 and 3 in eq 1 we have,

$$\left.\begin{aligned} Ld^2Q_1/dt^2+RdQ_1/dt+Q_1/C+Q_1/C_g-Q_2/C_g+h_1/C_g&=0\\ -Q_1/C_g+Q_2/C_g-h_1/C_g+Ld^2Q_2/dt^2+RdQ_2/dt+Q_2/C&\\ +Q_2/C_g-Q_3/C_g+h_2/C_g&=0\\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots&\\ -Q_{s-1}/C_g+Q_s/C_g-h_{s-1}/C_g+Ld^2Q_s/dt^2+RdQ_s/dt+Q_s/C&\\ +Q_s/C_g-Q_{s+1}/C_g+h_s/C_g&=0\\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots&\\ -Q_{n-1}/C_g+Q_n/C_g-h_{n-1}/C_g+L_nd^2Q_n/dt^2+R_ndQ_n/dt+Q_n/C_n&=0 \end{aligned}\right\} \tag{5}$$

Now make the usual exponential substitution

$$Q_s=d_s+A_se^{-\lambda t} \tag{6}$$

where d_s, A_s, and λ are constants, as yet undetermined.[2] Applying eq 6 to the typical equation of eq 5 we obtain,

$$\begin{aligned} &-h_{s-1}-d_{s-1}+[-A_{s-1}+(C_gL\lambda^2-C_gR\lambda+C_g/C+2)A_s-A_{s+1}]e^{-\lambda t}\\ &+(C_g/C+2)d_s-d_{s+1}+h_s=0 \end{aligned}$$

This suggests that we define two new quantities

$$\left.\begin{aligned} w(\lambda)&=C_gL\lambda^2-C_gR\lambda+C_g/C+2\\ X(\lambda)&=C_gL_n\lambda^2-C_gR_n\lambda+C_g/C_n+1 \end{aligned}\right\} \tag{7}$$

Eq 5 then become

$$\left.\begin{aligned} [(w-1)A_1-A_2]e^{-\lambda t}&=-(C_g/C+1)d_1+d_2-h_1\\ [-A_1+wA_2-A_3]e^{-\lambda t}&=d_1-(C_g/C+2)d_2+d_3+h_1-h_2\\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots&\\ [-A_{s-1}+wA_s-A_{s+1}]e^{-\lambda t}&=d_{s-1}-(C_g/C+2)d_s+d_{s+1}+h_{s-1}-h_s\\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots&\\ [-A_{n-1}+XA_n]e^{-\lambda t}&=d_{n-1}-(C_g/C+1)d_n+h_{n-1} \end{aligned}\right\} \tag{8}$$

Since the constants d are at our disposal, we shall so choose them as to reduce the right-hand members of eq 8 to zero. The d's are therefore defined by the following equations,

---

[2] Strictly speaking there will be $2n$ λ's and Q_s will be of the form $Q_s=\sum_{k=1}^{2n}A_{sk}e^{-\lambda_k t}$. For the time being we shall omit the subscript k. Strickly speaking also A_s is not necessarily a constant. In case a given λ_r is a double root of the secular equation, that is, if the rth frequency component is critically damped, the corresponding A_{sr} is a linear function of time of the form $(At+B)$. See, for example, Ames and Murnaghan, Theoretical Mechanics, page 124 (Ginn and Co., 1929).

$$\left.\begin{aligned} (C_g/C+1)d_1-d_2&=-h_1\\ \cdots\cdots\cdots&\cdots\cdots\cdots\\ -d_{s-1}+(C_g/C+2)d_s-d_{s+1}&=h_{s-1}-h_s\\ \cdots\cdots\cdots&\cdots\cdots\cdots\\ -d_{n-1}+(C_g/C+1)d_n&=h_{n-1} \end{aligned}\right\} \qquad (9)$$

With the d's having the values determined by eq 9 the solution of eq 8 reduces to the solution of the following equations:

$$\left.\begin{aligned} (w-1)A_1-A_2&=0\\ -A_1+wA_2-A_3&=0\\ \cdots\cdots\cdots&\cdots\\ -A_{s-1}+wA_s-A_{s+1}&=0\\ \cdots\cdots\cdots&\cdots\\ -A_{n-1}+XA_n&=0 \end{aligned}\right\} \qquad (10)$$

The condition that a solution other than zero shall exist for the A's requires, as usual, that the determinant of the coefficients shall vanish. Let us call this determinant D_n. The condition for a solution then reduces to

$$D_n=\begin{vmatrix} w-1 & -1 & 0 & \cdots\cdots & 0 & 0\\ -1 & w & -1 & \cdots\cdots & 0 & 0\\ 0 & -1 & w & \cdots\cdots & 0 & 0\\ \cdots & \cdots & \cdots & \cdots\cdots & \cdots & \cdots\\ 0 & 0 & 0 & \cdots\cdots & w & -1\\ 0 & 0 & 0 & \cdots\cdots & -1 & X \end{vmatrix}=0 \quad n\text{th order} \qquad (11)$$

Let us also define

$$H_n=\begin{vmatrix} w & -1 & 0 & \cdots\cdots & 0 & 0\\ -1 & w & -1 & \cdots\cdots & 0 & 0\\ 0 & -1 & w & \cdots\cdots & 0 & 0\\ \cdots & \cdots & \cdots & \cdots\cdots & \cdots & \cdots\\ 0 & 0 & 0 & \cdots\cdots & w & -1\\ 0 & 0 & 0 & \cdots\cdots & -1 & X \end{vmatrix} \quad n\text{th order} \qquad (12)$$

Expanding D_n on its first column, we obtain

$$D_n=(w-1)H_{n-1}-H_{n-2} \qquad (13)$$

Expanding H_n similarly, we obtain

$$H_n=wH_{n-1}-H_{n-2} \qquad (14)$$

The method of handling such difference equations and the application of the results to electrical problems has been discussed by Wheeler and Murnaghan.[3] Let us make the trial substitution $H_n=cx^n$, where c is any constant. Substituting in eq 14 we obtain

$$x^2-wx=-1$$

whence

$$x=w/2\pm[w^2/4-1]^{1/2}$$

This suggests the substitution

$$w/2=\cosh\phi \qquad (15)$$

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[3] H. A. Wheeler and F. D. Murnaghan, Phil. Mag. [7] 6, 146-174 (July 1928).

Making this substitution, we obtain

$$x=\cosh\phi\pm\sinh\phi=e^{\pm\phi}$$

Hence

$$H_n=cx^n=ce^{\pm n\phi}$$

or

$$H_n=c_1\cosh n\phi+c_2\sinh n\phi$$

The values of c_1 and c_2 may be determined from the values assumed by H_n when $n=0$ and $n=1$. From eq 12 and 14 we have $H_2=wX-1=wH_1-H_0$.
Therefore

$$H_0=1$$
$$H_1=X$$

Using these values we readily find

$$c_1=1$$
$$c_2=\frac{X-\cosh\phi}{\sinh\phi}$$

so that

$$H_n=\frac{X\sinh n\phi-\sinh(n-1)\phi}{\sinh\phi} \tag{16}$$

And finally

$$D_n=\frac{X\cosh(n-1/2)\phi-\cosh(n-3/2)\phi}{\cosh\phi/2} \tag{17}$$

The problem of solving eq 10 is therefore reduced to the problem of finding those values of ϕ which will reduce eq 17 to zero. There will be n such values of ϕ corresponding to the n degrees of freedom of the system. Exact solutions for ϕ will be found only for certain special values of the constants R_n, L_n, and C_n, but approximate solutions can always be made.

Values of λ are obtained by substituting these values of ϕ in eq 7 and (15), from which we obtain

$$\lambda_{k,1},\lambda_{k,2}=R/2L\pm[R^2/4L^2-1/CL+(4/C_eL)\sinh^2\phi_k/2]^{\frac{1}{2}} \tag{18}$$

there being n values of k corresponding to the n possible values of ϕ.

It can now be verified by direct substitution that eq 10 will be satisfied for all possible values of ϕ if the A's are of the form

$$A_s=P_k\cosh(s-1/2)\phi_k \tag{19}$$

where the P_k are constants.
Therefore, the final solution of eq 5 is of the form

$$Q_s=d_s+\sum_k[P_{k,1}e^{-\lambda_{k,1}t}+P_{k,2}e^{-\lambda_{k,2}t}]\cosh(s-1/2)\phi \tag{20}$$

The constant d_s is evaluated from eq 9 and the constants $P_{k,1}$ and $P_{k,2}$ are determined by the initial conditions, that is, by the values of Q_s and i_s at $t=0$. With the evaluation of these constants the problem is completely solved, for with the aid of eq 20 we can now compute the voltage drop across any element of the circuit of figure 1 as an explicit function of time.

3. ILLUSTRATIVE CASE, EXACT SOLUTION

The application of the preceding formula is best illustrated by means of a specific example. For simplicity, a case has been chosen in which an exact solution is possible. Other special cases leading to exact solutions can be discovered with little difficulty. These exact solutions may be found to be of little practical importance since the constants of the terminal mesh, including as they do the constants of the apparatus under test, cannot in general be chosen arbitrarily.

Referring to figure 1, let us assume that

$$R_n=R,\ L_n=L,\ C_n=\frac{CC_g}{C+C_g}$$

This is assuming that the terminal section is identical with the typical section, the capacitance C_n being replaced by a capacitance C in series with a capacitance C_g. Substituting these values in eq 7 we find

$$X=w=2\cosh\phi$$

Substituting this value in eq 17, we find

$$D_n=\frac{\cosh\,(n+1/2)\phi}{\cosh\,\phi/2}$$

The condition for a solution is that $D_n=0$, or

$$\frac{\cosh\,(n+1/2)\phi}{\cosh\,\phi/2}=0$$

Hence $$\phi_k=\frac{2k+1}{2n+1}\pi i$$

or, if $i\theta=\phi$ $$\theta_k=\frac{2k+1}{2n+1}\pi, k=o,1,2,3,\ \ldots\ n-1 \qquad (21)$$

Referring to eq 18, we have

$$\lambda_{k,1},\lambda_{k,2}=R/2L\pm[R^2/4L^2-1/CL-(4/C_gL)\sin^2\theta_k/2]^{1/2} \qquad (22)$$

Three cases are to be distinguished, as usual, depending upon whether the radical of eq 22 is real, zero, or imaginary. In the first case (R greater than necessary for critical damping) the amplitude substitutions will be as given in eq 20. In the second case (R equal to the critical damping resistance for a given frequency) the substitution will be of the form (See footnote 2, page 588.)

$$(P_{r,1}t+P_{r,2})e^{-\lambda_r t}\cos\,(s-1/2)\theta_r.$$

In the third case (R less than that necessary for critical damping) the λ's will be of the form

$$\lambda_k=\mu\pm 2\pi i\nu_k$$

where $$\mu=R/2L$$

$$2\pi\nu_k=[-R^2/4L^2+1/CL+(4/C_gL)\sin^2\theta_k/2]^{1/2} \qquad (23)$$

In this case the substitution corresponding to eq 20 will be of the form

$$P_k\cos\,(s-1/2)\theta e^{-\mu t}\cos\,(2\pi\nu_k t-\alpha_k),$$

where P_k and α_k are now the unknown constants.

Suppose now that the value of R is such as to critically damp the rth frequency component. We can then write a general expression for the charge on the sth capacitor in the following form:

$$\left.\begin{aligned} Q_s = d_s + \sum_{k=0}^{r-1}(P_{k,1}e^{-\lambda_{k,1}t} + P_{k,2}e^{-\lambda_{k,2}t}) \cos\,(s-1/2)\theta_k \\ + (P_{r,1}t + P_{r,2})e^{-\lambda_r t} \cos\,(s-1/2)\theta_r \\ + \sum_{k=r+1}^{n-1} P_k \cos\,(s-1/2)\theta_k e^{-\mu t} \cos\,(2\pi\nu_k t - \alpha_k). \end{aligned}\right\} \quad (24)$$

The $2n$ constants are determined from the initial conditions, that is at $t=0$,

$$Q_s = Q_{s,0}$$
$$i_s = i_{s,0}$$

The problem of determining these $2n$ constants is the standard problem of passing an n term trigonometric sum through n arbitrarily chosen points. If the n points are equally spaced (that is, if the solution of eq 17 yields exact values of θ of the form $\theta = \frac{k\pi}{n}, \frac{2k+1}{2n+1}\pi$, etc.) the solutions can be written down immediately.[4] The condition that $Q_s = Q_{s,0}$ at $t=0$ leads to the solutions of the following identical form for $\left(P_{k,1}+P_{k,2}\right)$, $P_{r,2}$, and $P_k \cos \alpha_k$ (for the case where $\theta_k = \frac{2k+1}{2n+1}\pi$)

$$P_k \cos\,\alpha_k = 4/(2n+1)\sum_{s=1}^{n}(Q_{s,0} - d_s) \cos\,(s-1/2)\theta_k. \quad (25)$$

The second initial condition, $i_s = i_{s,0}$ at $t=0$, leads to similar solutions for the same pairs of constants, from which the individual constants can be evaluated. If the initial conditions are known the summations of eq 25 can always be carried through and the constants determined.

The exact determination of these initial conditions is a matter of some difficulty in the case of a surge-voltage generator. It is not correct to assume that at time zero all charges are equal and all currents zero, although this represents the limiting case of all gaps closing simultaneously. Actually, the breakdown of the gaps is successive, and the initial time for the whole system should be taken as the moment of breakdown of the last gap. At this moment the charges on the preceding capacitors are not identical and the currents in the preceding meshes are not zero. To compute the initial conditions exactly the following procedure must be followed. First, compute the voltage above ground of the terminal of the second section of the generator (that is, point a, fig. 1) after the first gap has been closed and before the second gap has broken down. This computation can be carried out exactly since there is only one gap in this circuit and it is arbitrarily closed at time zero, at which time both initial charges are equal and both initial currents are zero. Now, having a knowledge of the voltage at which the second gap will break down, or having made a reasonable assumption as to that voltage, we compute the charges and currents existing at the moment that break-

[4] W. E. Byerly, Fourier's Series and Spherical Harmonics, chapter II. (Ginn and Co., 1895.)

down voltage is reached at the second gap. This moment is taken as the new origin of time measurement in dealing with the three-section network now in the circuit, and these charges and currents are the required initial conditions. We repeat the above process for the third gap and for each of the other gaps in turn until finally we are able to compute all the charges and all the currents at the moment of breakdown of the last gap. It is readily seen that the rigorous computation of the voltage across the terminals of an n-section generator becomes very laborious if n is very large, say 20 or 30.

To make these ideas somewhat more specific, sample calculations have been carried out on a three-section network having the following circuit constants:

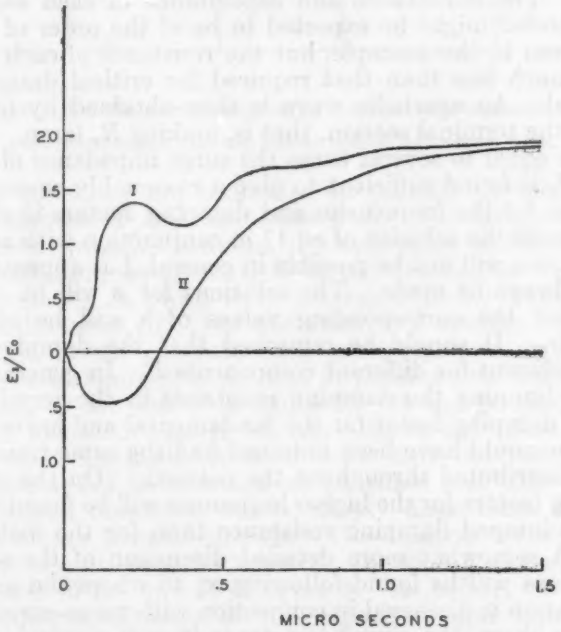

FIGURE 2.—*Voltage surge of a two-section generator discharging into a previously uncharged terminal section.*

Curve *I*, both gaps closed simultaneously.
Curve *II*, second gap closed 1×10^{-7} seconds after first gap.

$$L = L_n = 5 \times 10^{-6} \text{ h.}$$
$$R = R_n = 40.5 \text{ ohms.}$$
$$C = 0.25 \times 10^{-6} \text{ farads.}$$
$$C_g = 0.25 \times 10^{-8} \text{ farads.}$$
$$C_n = \frac{C\,C_g}{C + C_g}$$
$$E_0 = \text{initial charging voltage.}$$

The value of resistance used is just sufficient to critically damp the fundamental of the three-section network. We have here a two-section generator discharging into a previously uncharged terminal circuit.

In figure 2 are plotted curves of E_3/E_0 against time, E_3 being the voltage across the capacitor C_g in the terminal circuit. Curve *I* is plotted for the limiting case in which both gaps are closed simultaneously. Curve *II* is plotted for the case in which the second gap closes 0.1 microsecond after the first gap. In this time, the voltage across the second gap will have risen to about 1.25 E_0. The difference between these curves indicates the importance of initial conditions, that is, gap settings, on the shape of the voltage wave front.

4. DISCUSSION

In surge-voltage generators as used in practical work the situation is somewhat more complicated than is indicated in the simple example just cited. The inductance and capacitance of each section of an actual generator might be expected to be of the order of magnitude of those given in the example, but the resistance of each section, R, might be much less than that required for critical damping of the fundamental. An aperiodic wave is then obtained by inserting resistance in the terminal section, that is, making R_n large. Ordinarily a resistance equal to several times the surge impedance of the circuit $(L_{\text{total}}/C_1)^{1/2}$, is found sufficient to give a reasonably smooth wave.[5]

A solution for the frequencies and damping factors is obtained, as before, through the solution of eq 17 in conjunction with eq 7 and 15. Exact solutions will not be possible in general, but approximate solutions can always be made. The solutions for ϕ will be of the form $\phi=x\pm iy$ and the corresponding values of λ will be of the form $\lambda_k=\mu_k\pm 2\pi i\nu_k$. It should be remarked that the damping constant μ_k is now different for different components k. In general, it will be found that lumping the damping resistance in the terminal section results in a damping factor for the fundamental and lower harmonics greater than would have been obtained had the same resistance been uniformly distributed throughout the network. On the other hand, the damping factors for the higher harmonics will be found to be much less for the lumped damping resistance than for the distributed resistance. A somewhat more detailed discussion of the solutions of such equations will be found following eq 46 where the solution of a similar equation is discussed in connection with surge-current circuits. As is shown there, the circuit constants in any particular case may suggest valid simplifications and approximations which greatly facilitate the computations.

Exact solutions for the amplitude factors P_k, see eq 20, cannot be obtained in general. With a knowledge of the proper form of solution, however, and the correct values of the λ's, it will be possible to compute, by the ordinary methods of wave analysis, the amplitude factors P_k necessary to fit a given surge-voltage oscillogram. Even this meager information may prove valuable, however. It will enable one, from data obtained on the well-defined crest and tail of a voltage wave, to reproduce the sharply rising front of the voltage wave which is actually of much importance but is often poorly defined on the oscillograms.

[5] P. L. Bellaschi, Trans. Am. Inst. Elec. Engrs. 51, 936–945 (1932).

III. SURGE-CURRENT GENERATOR

1. STATEMENT OF THE GENERAL PROBLEM

The problem to be solved in connection with some types of the surge-current generator can be stated conveniently in terms of the simplified circuit shown in figure 3. The n identical capacitors com-

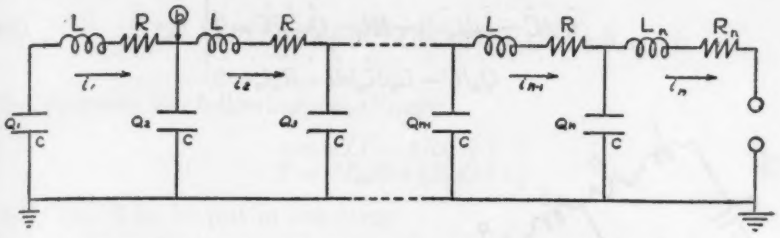

FIGURE 3.—*Schematic diagram of a surge-current generator.*

The charging circuits have been omitted to avoid confusing the figure.

prising this generator are connected in parallel by identical leads having resistances R and inductances L. The nth, or terminal, mesh, which in practice contains the apparatus under test as well as other measuring equipment, is closed through a resistance R_n and an inductance L_n which is, in general, different from the resistance and inductance (R, L) of the other $n-1$ meshes. As actually used, a surge-current generator will consist of two or more units, such as shown in figure 3, connected in parallel to a common sphere gap and load, as are shown in figure 4.[6] If the parallel circuits of figure 4 are identical, and if we can neglect the effect of mutual inductance between leads, it is obvious that the currents in the parallel circuits will be identical at all times and that the current through the load resistance will be simply three times that flowing in any one of the parallel circuits. The solution for the case of a symmetrical circuit, such as figure 4, therefore reduces essentially to the solution of the circuit of figure 3. As before, we neglect the internal structure, if any, of the capacitors and represent their internal losses by a suitable series resistance, and neglect the change of resistance of the leads with frequency. If identical charges Q_0 are placed on each of the capacitors and the nth mesh is then closed through its inductance and resistance, it is required to find the charges on the various capacitors and the currents in the various meshes as explicit functions of time. We are particularly interested here in the current in the nth mesh. The method of solution will closely parallel that used in connection with the surge-voltage generator in section II.

[6] P. L. Bellaschi, Elec. Eng. **53**, 86 (1934). K. B. McEachron and J. L. Thomason, Gen. Elec. Rev. **38**, 126 (1935).

2. FORMAL SOLUTION OF THE GENERAL PROBLEM

Referring now to figure 3 and writing down the equations for the summation of the voltages around each mesh we have, if Q_s is the charge on the sth capacitor and i_s the corresponding current:

$$\left.\begin{aligned} Q_1/C - L di_1/dt - Ri_1 - Q_2/C = 0 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ Q_s/C - L di_s/dt - Ri_s - Q_{s+1}/C = 0 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ Q_n/C - L_n di_n/dt - R_n i_n = 0 \end{aligned}\right\} \tag{26}$$

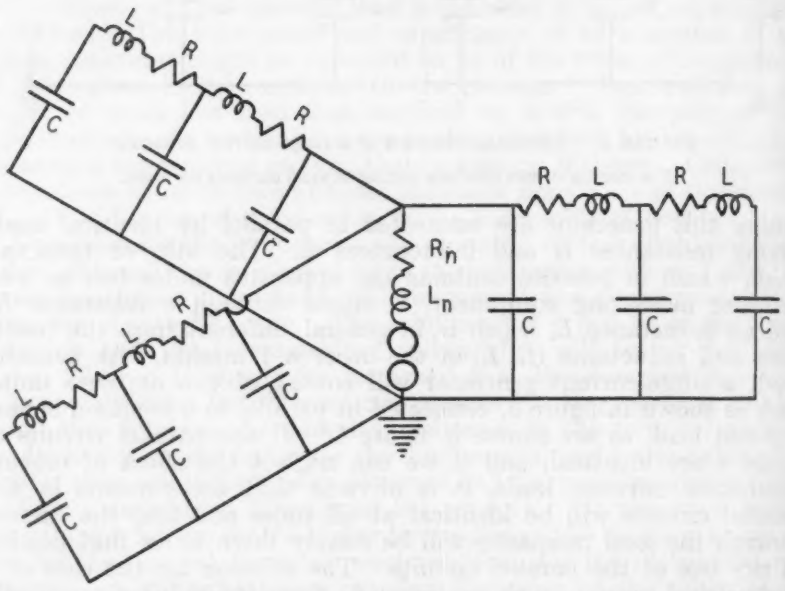

FIGURE 4.—*Schematic diagram of a surge-current generator using three identical circuits in parallel.*

Now, noting the currents at point b, we can write

$$i_1 = -dQ_1/dt$$

$$i_1 - i_2 - dQ_2/dt = 0$$

or

$$i_2 = -(dQ_1/dt + dQ_2/dt)$$

and, in general,

$$i_s = -\sum_{r=1}^{s} dQ_r/dt. \tag{27}$$

Let us now make the usual exponential substitution

$$Q_s = B_s e^{-\lambda t} \tag{28}$$

where B_s and λ are undetermined constants (see footnote 2, p. 588).

Substituting eq 27 and 28 in the typical equation of eq 26 and making a few obvious rearrangements, we have

$$(\lambda^2 LC - \lambda RC)\sum_{r=1}^{s-1} B_r + (\lambda^2 LC - \lambda RC + 1)B_s - B_{s+1} = 0$$

This suggests the following definitions:

$$\left.\begin{aligned} u &= \lambda^2 LC - \lambda RC + 1 \\ Y &= \lambda^2 L_n C - \lambda R_n C + 1 \end{aligned}\right\} \tag{29}$$

Eq 26 can then be put in the form:

$$\left.\begin{aligned} uB_1 - B_2 &= 0 \\ (u-1)\sum_{r=1}^{s-1} B_r + uB_s - B_{s+1} &= 0 \\ (Y-1)\sum_{r=1}^{n-1} B_r + YB_n &= 0 \end{aligned}\right\} \tag{30}$$

The condition for a solution giving values for the B's other than zero is, as usual, that the determinant of the coefficients shall vanish. This nth-order determinant, which leads to the secular equation, we shall call F_n. The determinantal equation is:

$$F_n = \begin{vmatrix} u & -1 & 0 & \cdots & 0 & 0 \\ u-1 & u & -1 & \cdots & 0 & 0 \\ u-1 & u-1 & u & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ u-1 & u-1 & u-1 & \cdots & u & -1 \\ Y-1 & Y-1 & Y-1 & \cdots & Y-1 & Y \end{vmatrix} = 0 \quad n\text{th order.} \tag{31}$$

Let us also define the following determinant which is obtained on expanding F_n:

$$K_n = \begin{vmatrix} u-1 & -1 & 0 & \cdots & 0 & 0 \\ u-1 & u & -1 & \cdots & 0 & 0 \\ u-1 & u-1 & u & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ u-1 & u-1 & u-1 & \cdots & u & -1 \\ Y-1 & Y-1 & Y-1 & \cdots & Y-1 & Y \end{vmatrix} \quad n\text{th order.} \tag{32}$$

Expanding eq 31 on the first row, we obtain

$$F_n = uF_{n-1} + K_{n-1}$$

Expanding eq 32 on the first row, we obtain

$$K_n = (u-1)F_{n-1} + K_{n-1}$$

whence

$$\begin{aligned} K_{n-1} &= -F_{n-2} + (uF_{n-2} + K_{n-2}) \\ &= F_{n-1} - F_{n-2}. \end{aligned}$$

Therefore,

$$F_n = (u+1)F_{n-1} - F_{n-2}. \tag{33}$$

Eq 33 is of exactly the same form as eq 14 and the method of solution of the two equations is identical. If we make the definition

$$(u+1)/2=\cosh \xi \tag{34}$$

we find that eq 33 can be put in the form

$$F_n=\frac{Y \sinh n\xi-\sinh (n-1)\xi}{\sinh \xi} \tag{35}$$

The problem of solving eq 26 is now reduced to the problem of finding those values of ξ which will reduce the right-hand member of eq 35 to zero. There will be n such values of ξ corresponding to the n degrees of freedom of the system.

Values of λ are obtained by substituting these values of ξ in eq 29 and 34 from which we obtain

$$\lambda_{k,1},\lambda_{k,2}=R/2L\pm\left[R^2/4L^2+(4/LC)\sinh^2\frac{\xi_k}{2}\right]^{\frac{1}{2}} \tag{36}$$

there being n values of k corresponding to the n possible values of ξ.

It can now be verified by direct substitution that eq 30 are satisfied for all possible values of ξ if the B's are of the form

$$B_s=U_k \cosh (s-1/2)\xi_k. \tag{37}$$

The final solution of our problem is therefore given by

$$Q_s=\sum_k[U_{k,1}e^{-\lambda_{k,1}t}+U_{k,2}e^{-\lambda_{k,2}t}] \cosh (s-1/2)\xi_k \tag{38}$$

and $i_s=-\sum_{r=1}^{s} dQ_r/dt$

where the U_k's are constants to be determined by the given initial values of charge and current.

3. ILLUSTRATIVE CASE, EXACT SOLUTION

The application of the preceding formulas is best illustrated by means of a specific example. For simplicity, a case has been chosen in which an exact solution is possible. Other special cases leading to exact solutions can be discovered with little difficulty.

Referring to figure 3, let us assume that

$$R_n=R \text{ and } L_n=L.$$

This is assuming that the terminal section is identical with the typical section. Substituting these values in eq 29 and 35, we obtain

$$Y=u=2 \cosh \xi-1$$

and

$$F_n=\frac{\cosh (n+1/2)\xi}{\cosh \xi/2}$$

and the condition for a solution, $F_n=0$, reduces to

$$\frac{\cosh (n+1/2)\xi}{\cosh \xi/2}=0 \tag{39}$$

Hence $$\xi_k=\frac{2k+1}{2n+1}\pi i$$

or, if $\xi=i\psi$ $$\psi_k=\frac{2k+1}{2n+1}\pi \tag{40}$$

$$k=0, 1, 2, \ldots n-1$$

Referring to eq 36 we have

$$\lambda_{k,1},\lambda_{k,2}=R/2L\pm\left[R^2/4L^2-(4/LC)\ \sin^2\frac{\psi_k}{2}\right]^{1/2}.$$

As before, we distinguish three cases depending upon whether R is greater than, equal to, or less than the value necessary to critically damp a given frequency. For values of R less than the critical damping value, we will have

$$\lambda_{k,1},\lambda_{k,2}=\mu\pm 2\pi i\nu_k$$

where $$\mu=R/2L \tag{41}$$

$$2\pi\nu_k=\left[-R^2/4L^2+(4/LC)\sin^2\frac{\psi_k}{2}\right]^{1/2}.$$

If now the value of R is such as to critically damp the rth frequency component, we can rewrite eq 38 in a form similar to eq 24.

$$\begin{aligned}Q_s=&\sum_{k=0}^{r-1}[U_{k,1}e^{-\lambda_{k,1}t}+U_{k,2}e^{-\lambda_{k,2}t}]\cos\ (s-1/2)\psi_k\\&+[U_{r,1}t+U_{r,2}]e^{-\lambda_r t}\cos\ (s-1/2)\psi_r\\&+\sum_{k=r+1}^{n-1}U_k\cos\ (s-1/2)\psi_k e^{-\mu t}\cos\ (2\pi\nu_k t-\beta_k).\end{aligned} \tag{42}$$

The constants U and β are determined, as before, by the initial conditions, which are, in this case at $t=0$

$$Q_s=Q_0$$

$$i_s=0$$

If R is less than the critical damping resistance for the fundamental, these conditions lead to the following values for the constants,

$$\beta_k=\tan^{-1}\mu/2\pi\nu_k \tag{43}$$

$$U_k=[(-1)^k 2Q_0/(2n+1)\cos\ \beta_k]\cot\frac{\psi_k}{2}$$

whence

$$Q_s=\sum_{k=0}^{n-1}(-1)^k[2Q_0/(2n+1)\cos\ \beta_k]\cot\frac{\psi_k}{2}\cos\ (s-1/2)\psi_k e^{-\mu t}\cos\ (2\pi\nu_k t-\beta_k)$$

and finally

$$i_s=2Q_0/(2n+1)(LC)^{1/2}\sum_{k=0}^{n-1}\sin\frac{\psi_k}{2}/\cos\ \beta_k\cdot\cot^2\frac{\psi_k}{2}e^{-\mu t}\sin 2\pi\nu_k t. \tag{44}$$

Let us assume, as a practical example, a generator having the following constants,

$$n=10,\ L=1\times10^{-6}h$$

$$C=2.4\times10^{-7}f,\ R=0.01 \text{ ohm}.$$

These constants approximate those that might be used in an actual generator. Using these data we find

$$\mu=5\times10^{3}$$

$$\nu_k=\frac{10}{2\pi}[1.67\sin^2(2k+1)\pi/42-25\times10^{-6}]$$

or

$$\nu_k\cong650\sin(2k+1)\pi/42 \text{ kc/s approx.}$$

$$k=0,\ 1,\ 2,\ .\ .\ .\ .\ .\ 9$$

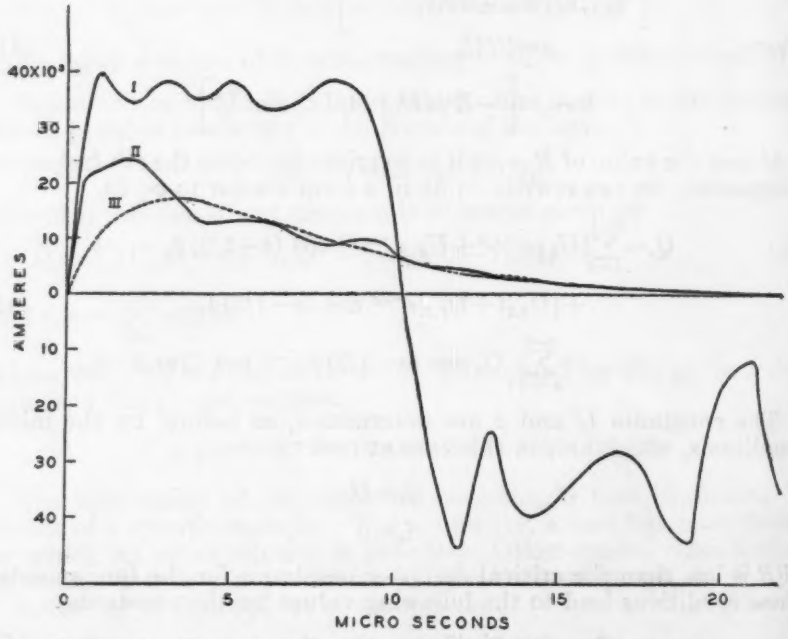

FIGURE 5.—*Current surge from a 10-section surge-current generator.*

Curve *I*, distributed resistance of 0.01 ohm per section, fundamental very much underdamped.
Curve *II*, distributed resistance of 0.61 ohm per section, fundamental critically damped.
Curve *III*, the critically-damped fundamental corresponding to curve *II*.

This gives a fundamental, ν_0, of 48.5 kc/s, which is to be compared with 32.4 kc/s, which would be computed by considering all the constants of the generator lumped and computing the resulting frequency.

In figure 5, curve *I*, i_n, the current in the terminal mesh, is plotted against time, using the circuit constants just given. In figure 5, curve *II*, i_n has been plotted for a generator having the same constants, except that $R=0.61$ ohm. This value of resistance is just sufficient to critically damp the fundamental. In this case μ (critical)$=30.4\times10^4$. Curve *III* represents the critically-damped fundamental for this case.

4. ILLUSTRATIVE CASE, APPROXIMATE SOLUTION

In actual practice it is customary to make the internal resistance of the generator (R) as small as possible and to achieve the necessary damping by making the terminal resistance (R_n) sufficiently large. These conditions allow certain simplifying assumptions to be made in the general solution of eq 35. It is well known, and can be verified in the numerical example of the last section, that if the damping factor is small, the damping affects the frequency as a second-order correction only. Neglecting the internal resistance of the generator for the moment, we have, from eq 29 and 34,

$$\lambda = \pm 2/(LC)^{1/2} \cdot \sinh \xi/2 \tag{45}$$

and eq 35 then becomes

$$\frac{\cosh (n-1/2)\xi + [2L_n/L \cdot \sinh \xi/2 \mp R_n(C/L)^{1/2}] \sinh n\xi}{\cosh \xi/2} = 0 \tag{46}$$

This equation can be solved approximately by any one of the standard methods. Its roots will be of the form

$$\xi_k = x_k \pm iy_k$$

and the λ's will be of the form

$$\lambda_{k,1}, \lambda_{k,2} = \pm 2/(LC)^{1/2} \cdot \sinh \frac{\xi_k}{2} = \mu_k \pm 2\pi i \nu_k,$$

and we have, in addition, the small damping arising from the internal resistance $\mu_o = \mathrm{R}/2\mathrm{L}$.

If we make the additional assumption that $L_n = L$, that is, that we add pure resistance only to the terminal section, eq 46 simplifies to

$$\frac{\cosh (n+1/2)\xi \mp R_n(C/L)^{1/2} \sinh n\xi}{\cosh \xi/2} = 0 \tag{47}$$

Approximate solutions can be written down for two limiting cases

$$R_n \text{ very small } \xi_k = \frac{2k+1}{2n+1}\pi i \quad k = 0, 1, 2, \ldots n-1$$

$$R_n \text{ very large } \xi_k = \frac{k}{n}\pi i \qquad k = 1, 2, \ldots . n-1$$

Taking one of these approximations as a value of iy above, we can enter eq 47 and find approximate values for x_k. Using these values of x_k, we can now compute a second approximation to the true values of y_k. This process may be repeated if necessary. The value of y corresponding to $k=0$ may sometimes have to be obtained by a separate evaluation. If we wish to find the value of R_n necessary to critically damp the fundamental, we solve equation 47 graphically under the assumption that y_0 is a small quantity the squares of which can be neglected and find that value of R_1 which just causes y_0 to vanish.

Sample calculations have been carried out on the 10-section generator of the last section under the conditions $L_n=L$, $R=0.01$ ohms, $R_n=2.3$ ohms (critical damping for the fundamental). In figure 6 are plotted, as solid lines, the damping factors, μ_k, for this case against the corresponding frequencies. As dotted lines are also plotted, the corresponding damping factors against frequency for the case of the same generator, the fundamental of which is critically damped by distributed resistance, $R=R_n=0.61$ ohm.

It should be remarked that had we considered the constants of this generator to be lumped, we would have computed a terminal resistance

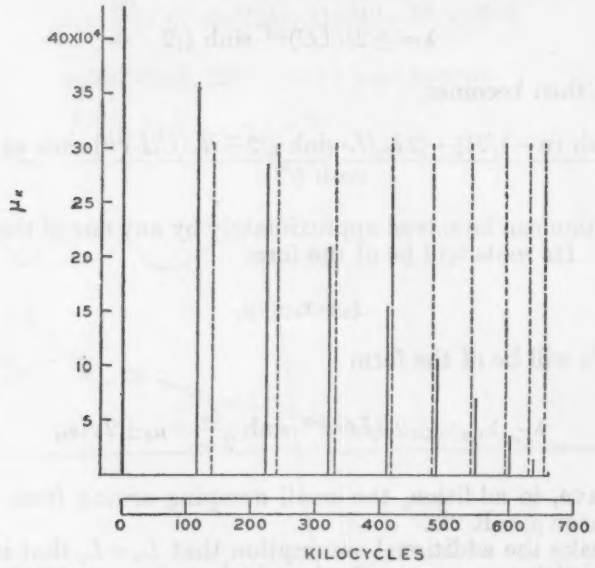

FIGURE 6.—*Damping factors against frequencies for a 10-section surge-current generator.*

Solid lines, damping factors against frequencies for the case of a lumped terminal resistance just sufficient to critically damp the fundamental. $R=0.01$ ohm, $R_n=2.3$ ohms.

Dotted lines, damping factors against frequencies for the case of a distributed resistance just sufficient to critically damp the fundamental. $R=R_n=0.61$ ohm.

of 4.1 ohms necessary to critically damp the system. The damping resistance obtained from the present closer calculations, that is 2.3 ohms, is in reasonable agreement with the experimental values observed on just such a generator, that is 1.5 to 2.0 ohms.[7]

IV. CONCLUSION

It is thus seen that the mathematical theory of surge-generators presents no essential difficulties, and that it is possible to set up complete formal solutions for both the surge-voltage and the surge-current generator which take account both of the internal structure of the generator and of the load to which it is connected. From these solutions it is possible to obtain exact numerical values for the damping factors and frequencies in certain special cases, and to obtain approximate values in all cases. Exact expressions for the amplitudes and phase angles can be obtained only in certain special cases.

[7] P. L. Bellaschi, Elec. Eng. 53, 86 (1934).

It has been the purpose of this discussion to outline the general method of attack on the mathematical problem presented by surge-generator circuits and the difficulties which will be met rather than to discuss in detail all the pecial cases which might be derived from the equations given above. If a particular generator were under consideration, many valid assumptions and approximations leading to useful approximate solutions might suggest themselves, which it would be fruitless to consider in a general discussion.

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EFFECTS OF CORRECTIONS FOR LIQUID - JUNCTION POTENTIALS OF SATURATED CALOMEL ELECTRODES ON DISSOCIATION CONSTANTS OBTAINED BY ELECTROMETRIC TITRATION

By Walter J. Hamer and S. F. Acree

ABSTRACT

Determiniations were made of the errors in pH, dissociation constants, "salting-out" coefficients, ionic strength, ionic concentrations, and hydrogen-ion activity coefficients arising from neglect or of partial corrections for the potential of the liquid junction between saturated potassium chloride (4.1 *N* KCl–HgCl electrode) and sodium malonate buffer solutions. The experimental data were obtained in the electrometric titration of 0.1 *M* malonic acid with 0.1007 *N* sodium hydroxide. It was shown that partial corrections produce a larger error in these quantities than no corrections. An error as small as 0.3 percent in pH may produce a change as large as 23 percent in dissociation constants.

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I. INTRODUCTION

Three types [1] of calomel electrodes are in accepted use as reference electrodes for the pH determination of unknown solutions. The remarks of this report will be confined to the saturated type. In its application, two sources of error in potential arise. The first is a liquid-junction potential produced by the contact of the KCl solution (contained in the calomel electrode) and the unknown solution; and the second is a liquid-junction potential introduced by the contact between the KCl solution and some solution of known pH, which has been employed in the calomel electrode calibration. These two potentials are usually of the same sign relative to the calomel electrode and may or may not be of the same numerical value. If the solution

[1] Saturated type (4.81 molal or 4.13 normal with respect to KCl). Normal type (mole KCl per liter of solution). Decinormal type (decimole KCl per 1,000 g of H_2O).

employed for calibration has nearly the same equivalent conductance (equal average ionic mobilities) at the same titratable concentration as the unknowns, these two sources of error are approximately equal. This condition is commonly assumed in routine pH measurements. When this assumption is made, the value 0.2458 v listed by Clark [1][2], or the more precise value 0.2454 v obtained by Scatchard [2] with activity corrections, is employed at 25° C for the potential of the saturated type of calomel electrode on the hydrogen scale. However, when this assumption cannot be justified or when pH values of an accuracy of 0.1 percent or better are desired, the errors from these two sources must be eliminated. These two sources of error are also present for the other two types of calomel electrodes, and a study of the liquid-junction potentials involved in their calibration and application is now being made.

II. METHODS USED IN MAKING CORRECTIONS FOR LIQUID-JUNCTION POTENTIALS

Various methods have been proposed for elimination of errors due to liquid-junction potentials. Corrections for one or the other source of error have been made, but rarely for both. Walpole [3] measured the 4.1 *N*, the 3.5 *N*, and the 1.75 *N* calomel electrode against acetic acid-sodium acetate buffer solutions and corrected for the liquid-junction potentials by the Bjerrum [4] extrapolation method. This leads to a value of 0.2507 v for the saturated calomel type at 18° C, or 0.2455 v at 25° C, if the temperature coefficient given by Clark [1] is employed. This value is in error owing, first, to the use of Bjerrum's extrapolation method for liquid-junction correction which has been shown to be open to criticism by Kline, Meacham, and Acree [5] whose work was recently confirmed by McBain and Betz [6]; second, to the use of 1.883×10^{-5} for the ionization constant of acetic acid at 18° C, whereas Harned and Ehlers [7] obtained 1.750×10^{-5} from extensive measurements of galvanic cells free of liquid-junction potentials; and, third, to the employment of Kohlrausch's [8] conductivity data for KCl and acetic acid data which have been more accurately determined by MacInnes and coworkers [9]. The extensively employed values of Britton, 0.2518 v [10]; Glasstone, 0.2426 v [11]; and Ingold and coworkers, 0.2449 v [12]; have been either partially corrected or left uncorrected for liquid-junction potentials. Moreover, the values of Britton and Ingold and coworkers, which are a function of ionization constants of weak electrolytes employed in the calomel electrode calibration, are also in error because these ionization constants have been determined by methods which are also subject to corrections for liquid-junction potentials. Glasstone's potential and ours (p. 607) agree fairly closely; a small part of the difference is due to the numerical values of the activity coefficient of the Cl^- ion and the normal potential of the silver-silver chloride electrode employed in the two treatments, and a larger part to Glasstone's neglect of interionic effects (E_f, defined in a following section).

To obtain these corrections, it is more satisfactory to employ some electrolyte which is completely dissociated, and whose stoichiometrical activity coefficient and pH value are known, in the calibration of the

[2] The numbers in brackets here and throughout the text refer to the numbered references at the end of this paper.

calomel electrode. HCl(0.1 *N*), which satisfies these three conditions, was used to great advantage by Scatchard [2]. From measurements and calculations of various galvanic cells, both with and without liquid junction, he obtained 0.2454 v at 25° C for the potential of the saturated calomel electrode on the hydrogen scale. However, this potential value contains the liquid-junction potential due to KCl (sat.) | 0.1 *N* HCl junction, the value of which at 25° C may be obtained from

$$E_D = -0.05915 \int t_i \, d\ln c_i$$

$$= -0.05915 \frac{C_1(U_1 - V_1) - C_2(U_2 - V_2)}{C_1(U_1 + V_1) - C_2(U_2 + V_2)} \log \frac{C_1(U_1 + V_1)}{C_2(U_2 + V_2)}, \qquad (1)$$

where the limits 1 and 2 refer to solution KCl (sat.) and HCl(0.1 *N*) respectively, and t_i and c_i represent, respectively, the ionic transference number and ionic concentration. For the second equality in equation 1 *C*, *U*, and *V* refer, respectively, to concentration in moles per liter, cationic mobility, and anionic mobility of electrolytes referred to in the limits. Upon substitution of the numerical values $C_1 = 4.13\ N$; $C_2 = 0.1\ N$; $V_1 = V_2 = 76.32$ [9]; $U_1 = 73.50$ [9]; and $U_2 = 349.72$ [9] in this equation, the value 0.00465 v is obtained for E_D. Scatchard [2] obtained 0.0047 v by his treatment. The above equation is that given by Henderson [13] for a "continuous mixture" solution junction and is based upon classical laws. However, the total potential at the solution junction is given by the integral

$$E_j = -0.05915 \int_1^2 t_i d\ln a_i = -0.05915 \int_1^2 t_i d\ln c_i - 0.05915 \int_1^2 t_i d\ln f_i \qquad (2)$$

or

$$E_j = -E_D - 0.05915 \int_1^2 t_i d\ln f_i = -E_D - E_f \qquad (3)$$

where the limits are the same as given in equation 1, a_i is the activity of the individual ions; c_i the ionic concentration; f_i the practical individual ionic activity coefficient; t_i the ionic transference number; and E_f, the second integral, corrects E_D for its deviation from classical dilution laws due to interionic effects. The numerical value of E_f may be evaluated by the graphical method of Harned [14] for each ion involved at the boundary KCl (sat.) | HCl (0.1 *N*). This method gives −0.00074 v for H^+, −0.00245 v for Cl^-, and +0.00177 v for K^+, or a total value for E_f equal to −0.00142 v. Therefore, the value of the emf of the calomel electrode (sat. type) on the hydrogen scale becomes equal to $(-E_0 - E_D - E_f)$ or numerically to 0.2422 v at 25° C.

In applications, it is a rather simple matter to employ the Henderson equation to calculate E_D, but the calculation of E_f by the above defined method is obviously complex. In addition, the latter modification is based upon several assumptions, namely, (1) calculation of ionic activity coefficients by the MacInnes [15] postulation of equality of activity coefficients of K^+ and Cl^- in KCl solutions; (2) uniform ionic diffusion at the boundary junction; and (3) accuracy of the graphical relation between the ionic activity coefficients and ionic transference numbers. In view of these assumptions and the complexity of the mathematical treatment, it is much more convenient

to disregard E_f. This disregard is not as serious as it might at first appear, since an E_f value must also be calculated for the junction KCl (sat.) | unknown and this value will oppose the value of −0.00142 v obtained above in the calibration. For example, in the titration of 0.1 *M* malonic acid by 0.1007 *N* sodium hydroxide, Burton, Hamer, and Acree [16] obtained −0.00203 v for E_f at the point where 1 ml of alkali had been added to 25 ml of acid. Therefore, for this point on the titration curve of malonic acid, the disregard of E_f produces an error of −0.00061 v. It must be emphasized at this point that this error is strictly relative, as one quantity, f_H (the practical activity coefficient of the hydrogen ion), depends upon the value assigned to E_f, and E_f depends upon a value assigned to f_H, which, in turn, depends upon the assumption that the emf corrected for E_0 and E_D gives the hydrogen-ion concentration; the magnitude of the error may be somewhat smaller than that calculated above depending upon the value initially assigned to one of these quantities. The important point is that these two E_f values are of the same sign and consequently to some extent counteract each other. The same general conclusions persist throughout the titration. Furthermore, the semithermodynamic equation for the emf at 25° C obtained in the measurement of the pH of an unknown is

$$E=E_0+E_D+E_f-0.05915 \log c_H f_H, \quad (4)$$

where E is the measured emf, E_0 is the potential of the saturated calomel electrode on the hydrogen scale, E_D and E_f as previously defined are in this case values for the liquid junction KCl (sat.) | unknown, c_H is the hydrogen-ion concentration, in moles per liter, and f_H is the practical activity coefficient of the hydrogen ion. Inspection of this equation shows that an additional factor, namely, $-0.05915 \log f_H$ must be considered. In the calibration, this was done by Scatchard [2], but for the unknown this correction opposes the negative difference (−0.00061 v) obtained by disregarding E_f; it is positive owing to the fact that the activity coefficients of most if not all electrolytes in dilute solutions are less than unity, with the resultant positive value for $-0.05915 \log f_H$, and the subsequent reduction in error produced by a disregard of E_f. The correction due to $-0.05915 \log f_H$ is a variable depending upon the concentration and is introduced into the calculations of the dissociation constants at each point on the titration curve.

In conclusion, therefore, pending additional study of the effects due to E_f, the value 0.2407 v is more useful and adaptable than 0.2422 v for the calomel electrode (sat. type) potential, providing the Henderson equation is employed for calculating the liquid-junction potential between the saturated KCl and the known buffers. If the latter equation is not employed, 0.2454 v is recommended for this potential.

III. APPLICATIONS OF CORRECTIONS

1. pH VALUES

When the saturated calomel electrode is employed for pH determinations, two distinct treatments are in common practise, namely, (1) no corrections for liquid-junction potentials are made and (2) liquid-junction potential corrections are made for the junction KCl (sat.)| unknown, in both of which 0.2454 v is employed at 25° C as

the normal electrode potential [16]. A third treatment, and one less subject to error and criticism, is one in which account is taken of all potentials due to solution contacts, including corrections upon the calomel half-cell, with use of 0.2407 v as its electropotential on the hydrogen scale. These three treatments may be illustrated by the data on malonic acid previously reported [16].

The pH values and hydrogen-ion concentrations at 25° C obtained by these three methods are given by the equations

$(E-0.2454)/0.05915 = -\log c_H = \text{pH}$ (without corrections); (5)

$(E-0.2454-E_D)/0.05915 = -\log c_H = \text{pH}$ (with buffer corrections); (6)

$(E-0.2407-E_D)/0.05915 = -\log c_H = \text{pH}$ (with total corrections); (7)

where E_D is the liquid junction potential between KCl (sat.) and the buffer. Owing to the small magnitude of c_H, the values for E_D are the same in equations 6 and 7 [16]. These values as well as pH values by equation 6 have been reported previously. The pH values calculated by equations 5 and 7 are, respectively, 0.05 and 0.08 unit higher than those obtained with the use of equation 6. The values of c_H obtained from these equations are used to calculate the data in tables 1 to 4 inclusive.

2. DISSOCIATION CONSTANTS FOR ENTIRE pH CURVE

Illustrative values of K_1^c and K_2^c, the dissociation constants without corrections for interionic attraction, obtained by the respective expressions $c_H c_{HAn}/c_{H_2An}$ and $c_H c_{An}/c_{HAn}$, corresponding to the three treatments, are given in table 1. The corresponding ionic strengths are also listed. The designating numbers refer to the pH equations from which the hydrogen-ion concentration was obtained. The corresponding values of the constants corrected for interionic attraction, K_1^a and K_2^a, as well as the hydrogen-ion activity coefficients, are given in table 2 in columns labeled according to the above method. These latter values were calculated from the equation

$$\log K_1^a = \log K_1^c + \log f_H - A\frac{\sqrt{\mu}}{1+\sqrt{\mu}} + \beta\mu \qquad (8)$$

and

$$\log K_2^a = \log K_2^c + \log f_H - 3A\frac{\sqrt{\mu}}{1+\sqrt{\mu}} + (\beta'-\beta)\mu, \qquad (9)$$

in which the "salting-out" terms β and β' for mono- and dibasic salts are provisionally assumed to be zero.

TABLE 1.—*Dissociation constants and ionic strengths for malonic acid at 25° C by the three methods*

0.1007 *N* NaOH	$K_1^c \times 10^3$ (5)[a]	$K_1^c \times 10^3$ (6)	$K_1^c \times 10^3$ (7)	μ (5)	μ (6)	μ (7)
	FIRST EQUIVALENT OF SODIUM HYDROXIDE					
ml						
0.00	1.95	2.56	1.75	0.01955	0.02229	0.01858
1.00	2.15	2.74	1.93	.02098	.02329	.02002
5.11	2.27	2.67	2.08	.02598	.02709	.02541
11.08	2.29	2.60	2.10	.03462	.03505	.03435
17.10	2.29	2.57	2.11	.04234	.04250	.04223
22.10	2.44	2.84	2.35	.04768	.04774	.04766
24.25	6.31	7.09	5.77	.04978	.04974	.04977

TABLE 1.—*Dissociation constants and ionic strengths for malonic acid at 25° C by the three methods*—Continued

SECOND EQUIVALENT OF SODIUM HYDROXIDE

	$K'_2\times10^4$ (5)	$K'_2\times10^4$ (6)	$K'_2\times10^4$ (7)			
25.36	1.99	2.20	1.82	0.05199	0.05201	0.05197
25.86	3.10	3.40	2.84	.05342	.05344	.05341
27.40	4.79	5.27	4.39	.05771	.05771	.05770
28.35	5.21	5.70	4.78	.06024	.06025	.06024
30.39	5.61	6.15	5.14	.06541	.06542	.06541
33.85	5.73	6.31	5.26	.07339	.07340	.07339
39.85	5.67	6.28	5.21	.08522	.08522	.08522
42.85	5.52	6.10	5.06	.09036	.09036	.09036
44.83	5.35	5.95	4.91	.09351	.09351	.09351

[a] The numbers given after the K and μ values refer to the equations and methods employed to calculate pH values.

TABLE 2.—*Dissociation constants and activity coefficients of the hydrogen ion for malonic acid at 25° C by the three methods*

FIRST EQUIVALENT OF SODIUM HYDROXIDE

0.1007 N NaOH	$K'_1\times10^3$ (5)[a]	$K'_1\times10^3$ (6)	$K'_1\times10^3$ (7)	f_H (5)	f_H (6)	f_H (7)
ml						
0.00	1.52	1.95	1.37	0.895	0.887	0.897
1.00	1.67	2.10	1.51	.901	.893	.903
5.11	1.79	2.08	1.64	.926	.920	.928
11.08	1.81	2.04	1.67	.949	.945	.951
17.10	1.82	2.04	1.67	.949	.945	.951
22.10	1.95	2.26	1.87	.982	.979	.982
24.25	5.04	5.66	4.61	.986	.986	.987

SECOND EQUIVALENT OF SODIUM HYDROXIDE

	$K'_2\times10^6$ (5)	$K'_2\times10^6$ (6)	$K'_2\times10^6$ (7)			
25.36	1.03	1.14	0.94	.990	.989	.990
25.86	1.59	1.75	1.46	.990	.991	.991
27.40	2.42	2.66	2.22	.993	.993	.994
28.35	2.60	2.85	2.39	.994	.994	.995
30.39	2.74	2.98	2.51	.996	.996	.996
33.85	2.73	2.99	2.51	.998	.998	.998
39.85	2.57	2.85	2.36	.999	1.0	.999
42.85	2.46	2.72	2.23	1.0	1.0	1.0
44.83	2.36	2.62	2.08	1.0	1.0	1.0

[a] The numbers given after the K and f_H values have the same significance as in table 1.

TABLE 3.—*Concentration of each ion and the unneutralized acid, ionic strengths and the primary and secondary dissociation constants of malonic acid at 25° C within the intermediate range*

0.1007 N NaOH	C_{Na_2An}	C_{NaHAn}	C_{H_2An}	μ	$K'_1\times10^3$	$K'_2\times10^6$
ml						
22.10	0.000868	0.046118	0.000602	0.04886	1.67	2.69
24.25	.001940	.046041	.000268	.05192	1.67	2.66
25.36	.003005	.044894	.000165	.05395	1.67	2.65
25.86	.003601	.044134	.000133	.05497	1.67	2.63
27.40	.005649	.041240	.000074	.05821	1.66	2.60
28.35	.007032	.039213	.000054	.06032	1.66	2.57
30.39	.010087	.034683	.000018	.06495	1.65	2.53

3. DISSOCIATION CONSTANTS FOR INTERMEDIATE RANGE OF pH CURVE

The values of the dissociation constants given in tables 1 and 2 for the first and second equivalent of sodium hydroxide were calculated upon the postulation that any part of the pH titration curve could be treated as though each acid group behaved like a monobasic acid, that is, that the neutralization of the first and second acid groups proceeded separately. That this is not true is evident from the high values obtained for K^c_1 and K^a_1 and the low values obtained for K^c_2 and K^a_2 for the middle portion of the titration curve. More complete data obtained by the method which embodies partial corrections for liquid-junction potentials were reported previously [16]. To obtain the constants for this intermediate range, use may be made of the method given previously [16]. At this point only the treatment which includes total corrections for liquid-junction potentials will be given. The average values of K^c_1 (4.26 to 21.10 ml of added alkali) and K^c_2 (31.85 ml to 44.83 ml of added alkali) were found to be, respectively, 2.10×10^{-3} and 5.16×10^{-6}. These were employed to calculate the concentrations of each ionic species and of the undissociated acid for the intermediate range (22.10 ml to 30.39 ml of added alkali) by the method previously reported [16]. Illustrative values obtained in this manner are given in table 3 in columns labeled according to the above method.

4. ERRORS INVOLVED

The values for each of the preceding quantities calculated by the third treatment (with total liquid-junction potential corrections) are accurate to within ± 0.10 percent; deviations are due to experimental errors and differences in the two E_f values. The errors produced in these quantities when no corrections are made will be designated ewc (errors without corrections) and the errors produced by partial corrections will be designated ebc (errors due to buffer corrections only). These errors are summarized in table 4.

TABLE 4.—*Summary of errors*

MINIMUM ERRORS

Quantity	ewc	ebc	Quantity	ewc	ebc
	Percent	*Percent*		*Percent*	*Percent*
emf	[a] −0.0013	[a] −0.0047	$f_H(K^c_1)$[d]	−0.10	−0.10
pH	−.30	−.70	$f_H(K^c_2)$[d]	±.00	±.00
K^c_1	+9.35	+22.87	C_{NaHAn}(IR)[c]		+.81
K^c_2	+16.67	+38.89	C_{Na_2An}(IR)[c]		−.62
K^a_1	+9.33	+22.78	C_{H_2An}(IR)[c]		−.43
K^a_2	+22.22	+36.60	β[b]	(+)	(−)
μ (K^c_1)[d]	+.03	+.09	($\beta'-\beta$)[b]	(−)	(−)
μ (K^c_2)[d]	±.00	+.01	K^c_1(IR)[c]		+23.95
μ (IR)[d]		−.66	K^c_2(IR)[c]		+10.74

MAXIMUM ERRORS

emf	[a] −.0023	[a] −.0047	$f_H(K^c_1)$[d]	−.22	−1.11
pH	−1.00	−4.20	$f_H(K^c_2)$[d]	−.10	−.20
K^c_1	+11.42	+46.28	C_{NaHAn}(IR)[c]		+1.04
K^c_2	+8.29	+20.60	C_{Na_2An}(IR)[c]		−1.49
K^a_1	+10.95	+42.34	C_{H_2An}(IR)[c]		+6.11
K^a_2	+22.88	+44.44	β[b]	(+)	(−)
μ (K^c_1)[d]	+5.20	+19.95	($\beta'-\beta$)[b]	(−)	(−)
μ (K^c_2)[d]	+1.96	+1.92	K^c_1(IR)[c]		+27.27
μ (IR)[c]		+.86	K^c_2(IR)[c]		+25.30

[a] Unit is volt.
[b] Sign only (magnitude can only be estimated).
[c] Not for the product, but for the quantity in parenthesis.
[d] Intermediate range (IR).

It is to be noted that in all cases partial corrections for the liquid-junction potentials produce a larger error than no corrections. This is due to the same sign of the potentials for the junctions KCl (sat.) | HCl (0.1 *M*), and KCl (sat.) | malonate buffers which oppose each other in the setup of galvanic cells for pH measurements. It is also to be noted that the difference in the minimum and maximum error for K^a is less than for K^c, and is due to the negative error in f_H and the positive errors in the β values, which is equivalent to a negative error in the activity coefficients of the malonate ions (Debye-Hückel-Guggenheim calculation [16]). Although the errors in pH are small (0.3 to 4.2%), the errors in the dissociation constants become as much as 46 percent. This emphasizes the fact that although pH values may be in error by a small percentage only, interpretations or values calculated from them may be far from the truth or the correct magnitude.

Another error, although expressed in sign only, leads to a serious misinterpretation. The "salting-out" coefficient, β, for monobasic salts has a positive value when all or no corrections are made, but partial corrections give this coefficient a negative value. For the same coefficient (β') for dibasic salts, the sign (−) remains the same for all three treatments, but ($\beta'-\beta$) is of less magnitude when all corrections are made.

IV. DISCUSSION

The true dissociation constants of malonic acid in the presence of sodium malonate salts when all corrections have been made are $K^a_1 = 1.67\times10^{-3}$ (NaHAn=0.016815 to 0.046526 *N*) and $K^a_2 = 2.51\times10^{-6}$ (Na_2An=0.010133 to 0.018250 *N* and NaHAn=0.035002 to 0.022835 *N*).[3] These are average values in the middle range of the titration of each acid group. They are equal to the true ionization constants (K_1 and K_2) in pure water only, providing β and ($\beta'-\beta$) have zero value. That this is not the case is evident from the slight decrease in K^a_1 values and slight increase in K^a_2 values, as the ionic strength decreases. Since β has been found to be positive and ($\beta'-\beta$) negative the true value of K_1 must be smaller than K^a_1 and K_2 must be larger than K^a_2, providing the trend found here persists from ionic strengths of 0.02 and 0.05, respectively, to zero ionic strength. The magnitudes of β and ($\beta'-\beta$) can only be estimated from these measurements, since in the titration a variable buffer ratio is present and extrapolations are made over too large a concentration range. The average value of K_1 obtained from conductivity measurements is 1.64×10^{-3} which agrees fairly well with 1.67×10^{-3} obtained here. Vogel and Jeffery's [16] value of 1.397×10^{-3}, obtained by conductivity, may be low owing to their introduced assumption of similarity of conductivity for the carboxyl and carbamyl groups because of the near identity in the parachors of these groups. Gane and Ingold's [12] value of 1.49×10^{-3} may be low because of the method they employed in elimination of liquid junction in their titration determination. The conductivity data for K_2 vary from 1.0 to 2.1×10^{-6} [16] (Wegscheider's [16] value of 10.0×10^{-6} excepted) and the electrometric data from 2.03 to 4.45×10^{-6} [10, 16]. This large discrepancy is due to three facts: (1) neglect of liquid-junction potentials in the

[3] These values may still contain a small error due to effects of E_f, and work on a method for measuring the pH of unknowns in which no liquid junction is present is now in progress. Other incidental errors which may influence these results are (1) method of junction formation, Guggenheim, J. Am. Chem. Soc. 52, 1315 (1930), and (2) heats of mixing at the junctions, Hamer, J. Am. Chem. Soc. 57, 662 (1935).

latter values; (2) neglect of interionic attraction effects in both methods; and (3) methods employed for extrapolation to obtain limiting ionic mobilities in the former case.

If the classical treatment corrected for activity as described previously [16] is employed K^a_1 becomes 1.5×10^{-3} and K^a_2 becomes 2.2×10^{-6}. K^a_1 is in poorer agreement with the average conductivity data but K^a_2 is in better agreement. However, this agreement cannot be used as a criterion for preference of this treatment because of reasons given previously [16], because of the quality of the data and because of the assumptions that must be employed in this classical treatment.

V. SUMMARY

The potential of the saturated type of calomel electrode free of liquid-junction potentials was found to be 0.2422 v on the hydrogen scale at 25° C. It was shown that the value 0.2407 v is a more useful and adaptable value for pH determinations of known buffers, providing the Henderson equation is subsequently employed for the evaluation of the liquid-junction potential between KCl (sat.) and the buffer.

Errors in pH, dissociation constants, ionic strength, signs of "salting-out" coefficients, and hydrogen-ion activity, due to neglect of or partial corrections for potentials of the liquid junctions were calculated for malonic acid at 25° C. It was found that partial corrections lead to larger errors than no corrections. It was also found that, although maximum errors in pH may be only 4.2 percent, the maximum errors in derived quantities (dissociation constants) may become as much as 46 percent.

The primary and secondary dissociation constants of malonic acid in sodium malonate buffer solutions at 25° C were found to be, respectively, 1.67×10^{-3} and 2.51×10^{-6} when total liquid-junction potential corrections are made. The relations of these values to those expected in pure water were discussed.

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DIMENSIONS OF JERUSALEM-ARTICHOKE COSSETTES

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ABSTRACT

Cossettes were prepared from jerusalem-artichoke tubers in an experimental slicer equipped with a commercial beet knife set 1.5 mm up and 4.5 mm back. The tubers were of a size at least as large as the present average, yet the mean length of all particles was 1.163 cm, which is less than 0.5 in. The class composed of fragments less than 1 cm in length comprised nearly 60 percent of the total number of particles, occupied more than 20 percent of the total displacement volume, and presented nearly 25 percent of the gross surface area. The class under 4 cm in length comprised 96 percent of the total number, occupied 81 percent of the total displacement volume, and presented 83 percent of the gross surface area. This indicates high resistance to the flow of flood liquid in batteries of commercial size. The gross external area of all particles was slightly in excess of 2 m^2/dm^3 of displacement volume, and equivalent to approximately 62.8 ft^2/ft^3. The mean thickness of the diffusion layers, estimated from the ideal and observed mean cross-sectional profiles of the cossettes and the results of wetting experiments, apparently was about 0.086 cm for the condition of complete establishment of diffusion gradients. These values are of importance in estimating the coefficient of diffusion for the polysaccharides of the tubers under the conditions of battery extraction, to be presented in a later paper.

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I. INTRODUCTION

The measurements reported in the present paper were made (1) for the purpose of appraising and indicating the physical quality to be expected of cossettes prepared from jerusalem-artichoke tubers, and (2) to obtain data for the estimation of the coefficient of diffusion of the polysaccharides of the tubers under the conditions of battery extraction. Each is a very important consideration in the design of equipment for the production of levulose from this source.

II. SUMMARY OF DIMENSIONS

Owing to their small size and knobby shape in the present state of development, jerusalem-artichoke tubers yield cossettes which are predominantly short. To appreciate quantitatively the shortness of experimental cossettes prepared from tubers of at least average size, the lengths of the slices are subjected to statistical analysis. The measured lengths of all the particles in a sample are grouped into classes differing successively by increments of 1 cm. Arbitrarily, particles less than 1 cm in length are considered "fragments"; those longer than 1 cm true cossettes. The relative magnitude of a class is stated as a percentage of the whole sample with respect to (a) the frequency or number of particles; (b) the displacement volume of the tuber substance; and (c) the external surface area of the component particles.

For example, the mean results (table 2) indicate that the fragments, of which the maximum length was 1 cm, roughly ⅜ in., accounted for more than 50 percent of the frequency, for nearly 25 percent of the external area, and for more than 20 percent of the displacement volume of the whole sample. The group between zero and 4 cm (1.57 in.) in length contained 96 percent of the total number of particles; 81 percent of the aggregate displacement volume; and 83 percent of the total external area of all particles. The cumulative relative magnitudes within this group, as separately estimated by two observers, are presented in table 1.

TABLE 1.—*Distribution of the classes under 4* cm *in length*

Class length less than—	Magnitude of class, basis of—		
	Frequency	Displacement volume	External area
cm	*Percent*	*Percent*	*Percent*
1	53 and 65	19 and 24	22 and 27
2	79 and 82	45 and 46	48 and 49
3	90 and 91	63 and 68	65 and 70
4	95 and 96	79 and 83	81 and 84

The data presented above indicate that artichoke cossettes prepared with ordinary beet slicers and treated in the conventional diffusion apparatus of commercial capacity probably would offer excessive resistance to the flow of the flood liquid. For this reason the projected large-scale extraction of the polysaccharides from jerusalem artichokes may require a form of apparatus and a shape of slices which are decidedly different from those employed at present in the extraction of sucrose from beets. Since a different shape of slices may involve important differences in the effective surface area and mean thickness of the diffusion layers, considerable effort has been devoted to the estimation of these factors in material such as that actually employed in the experimental extractions of the polysaccharides. These estimates are based mainly upon the same measurements as those from which the length distributions were appraised.

The measurements indicate that with the knife-setting stated below the mean surface area of the cossettes was approximately 2.06 m^2/dm^3

of displacement volume, and that the mean thickness of each limb of the cross-sectional profile of a cossette, assuming a symmetrical figure, was approximately 0.138 cm. Experiments with wetting the cossettes with flood liquid and draining indicate that the adherent film may have been approximately 0.017 cm in thickness, suggesting that after the diffusion gradients were fully established the mean thickness of diffusion layers may have been approximately 0.086 cm. These are the values assumed for the mean external area and the mean thickness of the diffusion layers, respectively, in the estimation of coefficients to be presented in a later paper.

III. APPARATUS

The slicer employed in the preparation of the cossettes has been described very briefly,[1] and its construction is illustrated in figure 1. In operation, washed tubers are placed in the hopper and forced into contact with the reciprocating beet knife by means of the hand-operated plunger, seen best in the plan view. The knife, 137 mm in width and having 30 divisions, was set 1.5 mm up and 4.5 mm back. With this setting and at a speed of 131 cutting strokes a minute the slicer had a capacity of about 3.7 kg/min, equivalent to 28 g at a stroke.

IV. EXPERIMENTAL DETAILS

1. LENGTHS OF COSSETTES

From a single batch of cossettes prepared in the manner described, two samples were taken at random and weighed. Observers *B* and *C* each measured and recorded the length of every particle of tuber substance in one of these samples. Each piece was grasped individually with the forceps and placed on a millimeter scale. The weights of the samples and the number and mean length of particles in each class of each sample are presented in table 2.

TABLE 2.—*Distribution of particles by length*

OBSERVER *B*, 36.5-GRAM SAMPLE

Class range	Particle distribution as observed in sample			Particle distribution per dm³ (equivalent in 1.040 kg)			Relative magnitude of class, basis of				Length, percent × mean length
	Mean length	Frequency	Total length	Frequency	Total class length	External area of class	Frequency	External area	Length or volume	Inverse cumulative volume	
mm	mm		mm		cm	cm³	*Percent*	*Percent*	*Percent*	*Percent*	
0- 9	3.94	232	915	6,610	2,608	5,617	65.2	27.6	23.8	100.0	94
10-19	13.95	59	823	1,681	2,345	4,273	16.6	20.9	21.4	76.2	299
20-29	23.38	29	678	826	1,932	3,418	8.2	16.8	17.6	54.8	412
30-39	31.93	20	639	570	1,821	3,184	5.6	15.6	16.6	37.2	530
40-49	43.11	9	388	257	1,106	1,917	2.5	9.4	10.1	20.6	435
50-59	56.00	4	214	114	610	1,053	1.1	5.2	5.6	10.5	311
60-69	63.00	3	189	86	538	926	.8	4.5	4.9	4.9	309
70-79	--------	0	--------	0	--------	--------	.0	--------	--------	--------	--------
0-79	10.80	356	3,846	10,144	10,959	20,388	100.0	100.0	100.0	--------	1,080

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TABLE 2.—*Distribution of particles by length*—Continued

FRAGMENTS

Class range	Particle distribution as observed in sample			Particle distribution per dm^3 (equivalent in 1.040 kg)			Relative magnitude of class, basis of				Length, percent × mean length
	Mean length	Frequency	Total length	Frequency	Total Class length	External area of class	Frequency	External area	Length or volume	Inverse cumulative volume	
mm	mm		mm		cm	cm^3	*Percent*	*Percent*	*Percent*	*Percent*	
0– 9	3.94	232	915	6,610	2,608	5,617	65.2	27.6	23.8	-------	94

COSSETTES

10–79	23.63	124	2,931	3,534	8,351	14,771	34.8	72.4	76.2	-------	1,801

OBSERVER *C*, 45.0-GRAM SAMPLE

0– 9	4.41	213	940	4,923	2,172	4,498	53.2	21.7	19.0	100.0	84
10–19	13.26	102	1,353	2,357	3,127	5,649	25.5	27.2	27.3	81.0	363
20–29	22.57	47	1,061	1,086	2,452	4,296	11.8	20.7	21.4	53.7	484
30–39	35.67	21	749	485	1,731	2,984	5.2	14.3	15.1	32.2	540
40–49	46.07	14	645	324	1,491	2,554	3.5	12.3	13.1	17.1	601
50–59	52.00	1	52	23	120	205	.3	1.0	1.1	4.1	55
60–69	-------	0	-------	0	-------	-------	.0	-------	-------	3.0	-------
70–79	74.00	2	148	46	342	581	.5	2.8	3.0	3.0	221
0–79	12.37	400	4,948	9,244	11,435	20,767	100.0	100.0	100.0	-------	1,237

FRAGMENTS

0– 9	4.41	213	940	4,293	2,172	4,498	53.2	21.7	19.0	-------	84

COSSETTES

10–79	21.43	187	4,008	4,321	9,263	16,269	46.8	78.3	81.0	-------	1,736

OBSERVERS *B*+*C*, 81.5-GRAM SAMPLE

0– 9	4.17	445	1,855	5,679	2,367	4,993	58.9	24.3	21.1	100.0	88
10–19	13.51	161	2,175	2,054	2,776	5,035	21.3	24.5	24.7	78.9	334
20–29	22.88	76	1,739	970	2,219	3,905	10.0	19.0	19.8	54.2	453
30–39	33.85	41	1,388	523	1,771	3,072	5.4	14.9	15.8	34.4	534
40–49	44.91	23	1,033	293	1,318	2,269	3.0	11.0	11.8	18.6	528
50–59	53.20	5	266	64	339	581	.7	2.8	3.0	6.8	161
60–69	63.00	3	189	38	241	412	.4	2.0	2.1	3.8	135
70–79	74.00	2	148	26	189	323	.3	1.5	1.7	1.7	124
0–79	11.63	756	8,793	9,647	11,220	20,590	100.0	100.0	100.0	-------	1,163

FRAGMENTS

0– 9	4.17	445	1,855	5,679	2,367	4,993	58.9	24.3	21.1	-------	88

COSSETTES

10–79	22.31	311	6,938	3,968	8,853	15,597	41.1	75.7	78.9	-------	1,760

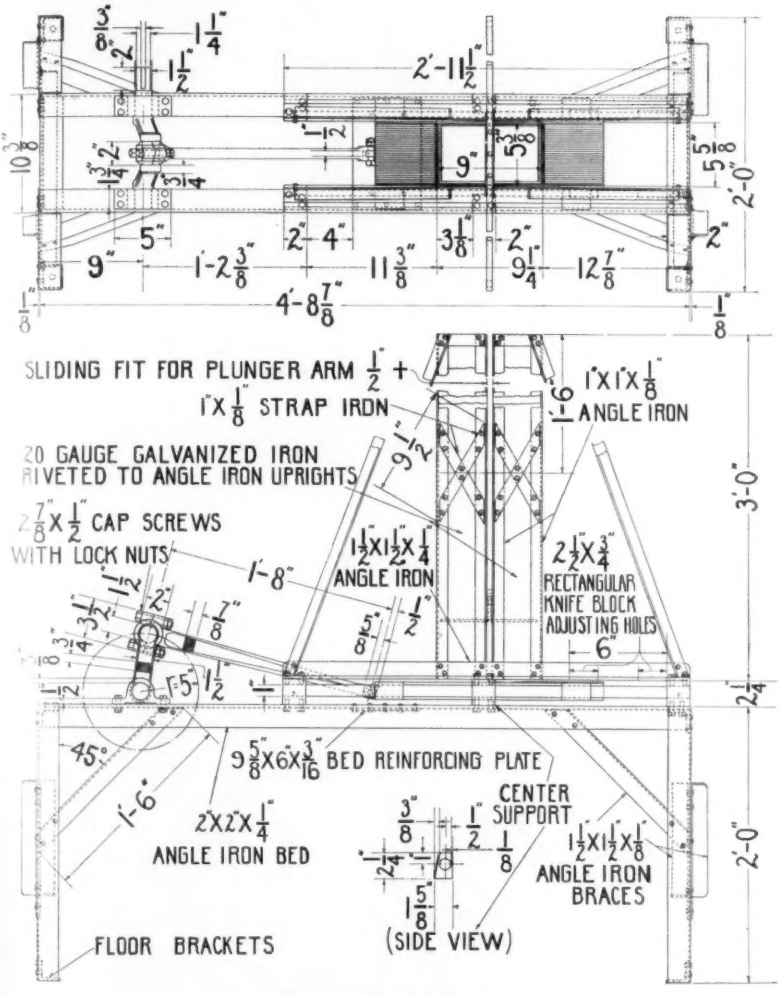

FIGURE 1.—*Slicer.*
Plan and side elevation.

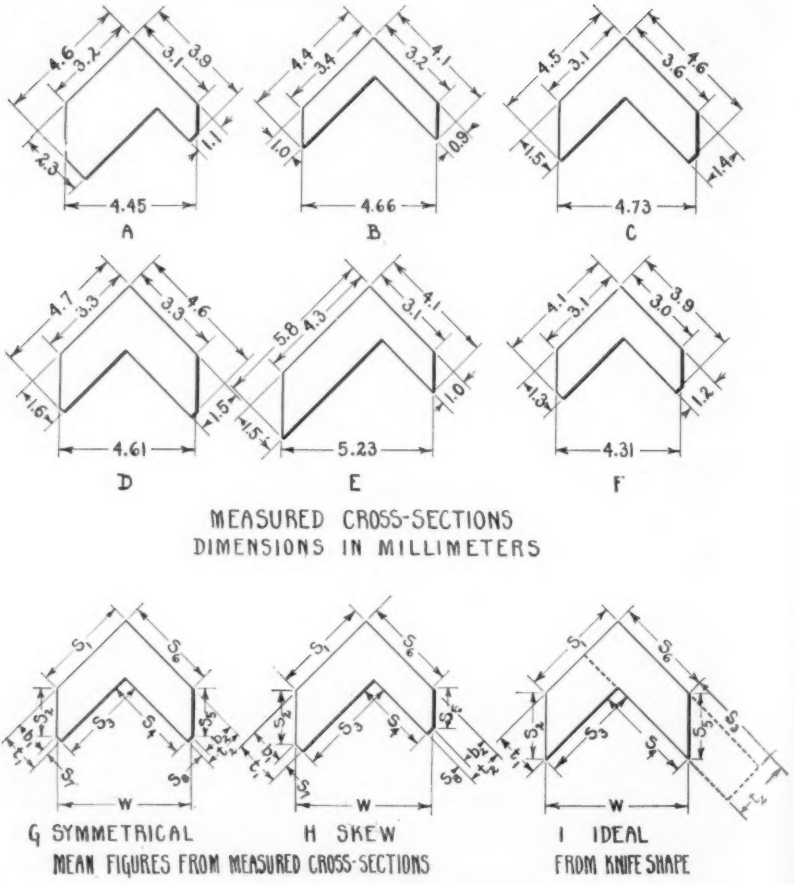

FIGURE 2.—*Cross-sectional profiles of cassettes.*

For dimensions of mean profiles see table 3.

2. CROSS-SECTIONAL PROFILES

The dimensions of the cross-sectional profiles were estimated by two methods, as follows:

(a) Several sections from each of six cossettes, taken at random from the same batch of cossettes as the length samples, were cut on a microtome and measured by observer *A* under a microscope with a calibrated ocular micrometer and a low-power objective. The mean values for each cossette are presented in sketches *A* to *F*, figure 2. All of the profiles are skew. The mean skew profile for the six cossettes is presented in sketch *H*, and the corresponding symmetrical profile in sketch *G*, figure 2.

(b) It was assumed that the mean cross-sectional profile of the chips in the length-measurement samples of observers *B* and *C* was of the ideal form presented in sketch *I*, figure 2, which is equivalent to the rectangle indicated by the broken outline, and that the width w was 0.457 cm as indicated by the dimensions of the knife. The corresponding mean thickness t was estimated from the total length of all the chips in the sample and the assumed density of 1.040 g/cm^3 as observed by *A* in three whole tubers taken at random from the lot from which the cossettes were prepared. As indicated in table 3, the results for the two observers differ from their mean by ± 2.2 percent, and their mean is identical with the thickness indicated for the mean symmetrical profile by method (a).

3. TOTAL LENGTHS AND FREQUENCIES

For observers *B* and *C* the total lengths and the frequencies in each class are taken directly from the recorded data. For observer *A* the total length of chips is assumed to have been that indicated by the mean cross-sectional area; the total number (for estimating the total area of ends) is assumed to have been equal to the mean of the counts by observers *B* and *C* (table 3).

4. EXTERNAL SURFACE AREAS

The areas of the external surfaces are estimated on the basis of the respective mean perimeters and the number of ends, supposed to have been two ends to a particle, each end equal in area to the calculated area of the mean cross-sectional profile. No correction is made for either roughness of surface or thickness of adhering film during diffusion. (See tables 2 and 3.)

5. VOLUMES OF CLASSES

The volume occupied by a class is assumed to have been proportional to the aggregate length of its particles; hence the percentage magnitude of a class by volume is also its percentage magnitude by total length (table 2).

6. IDEAL DENSITY OF PACKING

If cossettes of uniform and symmetrical profile could be packed into a battery cell in perfect criss-cross arrangement without distortion,

as suggested by the diagram for ideal packing in figure 3, the maximum density of filling would be attained when the vertical sides of each cossette were in contact with corresponding sides, or with the ends of adjacent cossettes, or else with the walls of the cell. In such a state of filling, the internal space of a cell would be occupied by a myriad of "prismatic elements" (fig. 3), each consisting partly of cossette substance and partly of space available for flood liquid. The part of the volumetric capacity of the cell which would be occupied by cossette substance would be indicated by the ratio of the cross-sectional area,

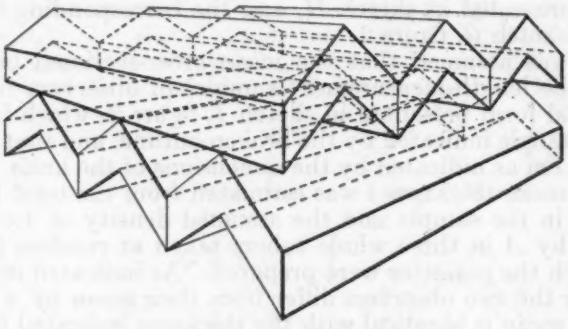

FIGURE 3.—*Arrangement of cossettes in ideal packing.*

a', of the cossette profile to the cross-sectional area, a, of the prismatic element, and

$$f'=\frac{100a'}{a} \tag{1}$$

would express the percentage of the whole capacity of the cell which would be devoted to the cossette substance. Since the space not occupied by cossette substance is available for flood liquid, inspection of the diagrams (figs. 2 and 3) indicates that the percentage of cell space available for flood liquid would be represented by the equation

$$f''=\frac{100s_1^2}{a} \tag{2}$$

when the cossettes have the ideal profile; and since $s_1=s_2$ and $w=2s_1\sqrt{2}$, the relation is easily checked algebraically. The correction to be applied when the mean profile has clipped corners is obvious. Since the percentage filling of the cells is indicated by the relation

$$f'=100-f'',$$

the calculated values for the hypothetical ideal filling of the cells, corresponding to the cross-sectional areas of the respective symmetrical profiles (ideal and mean), as presented in table 3, vary from 46 to 48, while the observed values for random packing as attained in actual extraction experiments varied from 44 percent to 63 percent and averaged 52 percent of the cell space.

TABLE 3.—*Estimated dimensions of jerusalem-artichoke cossettes*

[Values for observer *A* and method 1 refer to mean profiles *G* or *H*; all others to ideal profile *I*, figure 2]

Item and description	Symbol	As estimated by observer			Means for observers		
					$B+C$	$A+(B+C)$ by method	
		A	*B*	*C*		1	2
1. Cross-sectional area of one chip, cm²	a'	0.0906	0.0913	0.0875	0.0891	0.0896	0.0899
2. External surface area, cm²/dm³:							
a. Sides of chips	A_s	18,150	18,540	19,150	18,870	18,400	18,930
b. Ends of chips	A_e	1,750	1,850	1,620	1,720	1,730	1,730
Total	A	19,900	20,390	20,770	20,590	20,130	20,660
3. Density, g/dm³ at 20° C	d	1,040	1,040	1,040	1,040	1,040	1,040
4. Frequency, number of chips/dm³	F	9,650	10,140	9,240	9,650	9,650	9,650
5. Mean length, cm/chip	l	1.144	1.080	1.237	1.163	1.156	1.156
6. Total length, cm/dm³	L	11,040	10,960	11,430	11,220	11,160	11,160
7. Mean perimeter of profile, cm	p	1.644	1.691	1.675	1.682	1.649	1.696
8. Breadth of sides, cm, mean:							
a. Symmetrical, sketches *G*, *I*	s_1, s_2	.331	.323	.323	.323	.327	.327
b. Skew, sketch *H*	s_1	.340	------	------	------	.336	------
	s_2	.322	------	------	------	.318	------
a. Symmetrical, sketches *G*, *I*	s_3, s_4	.160	.199	.191	.195	.158	.194
b. Skew, sketch *H*	s_3	.179	------	------	------	.177	------
	s_4	.141	------	------	------	.139	------
a. Symmetrical, sketches G, *I*	s_5, s_6	.306	.323.	.323	.323	.307	.327
b. Skew, sketch *H*	s_5	.314	------	------	------	.363	------
	s_6	.301	------	------	------	.265	------
a. Symmetrical, sketches *G*, *I*	s_7, s_8	.025	------	------	------	.020	------
b. Skew, sketch *H*	s_7	.026	------	------	------	.026	------
	s_8	.020	------	------	------	.025	------
9. Thickness of limbs; cm:							
a. Symmetrical, sketches *G*, *I*	t_1, t_2	.138	.141	.135	.138	.132	.137
b. Skew, sketch *H*	t_1	.154	------	------	------	.151	------
	t_2	.119	------	------	------	.123	------
10. Percentage of flood space, hypothetical ideal	f''	53	53	54	54	52	54
11. Width of cossette profile, cm	w	.468	.457	.457	.457	.462	.462
12. "Spherical equivalent": [1]							
Radius, cm	r	.1507	------	------	.1457	.1490	.1452
Frequency/dm³	n	69,760	------	------	77,190	72,160	77,980
13. "Cubical equivalent": [1]							
Edge, cm	e	.3015	------	------	.2914	.2981	.2904
Frequency/dm³	n	36,490	------	------	40,410	37,750	40,830

[1] Number and dimensions of spheres or cubes, respectively, having the same surface area, in 1 dm³, as that estimated for the cossettes.

7. SIZE OF TUBERS

The tubers from which the samples of cossettes were prepared averaged about 50 g in weight, which is rather larger than the average weight of jerusalem artichokes as they occur in the present state of development. Moreover, they probably were not more knobby than the general run of tubers; yet the mean length of slices according to both counts was less than half an inch. The length distribution of the particles according to either count (table 2) indicates that cossettes cut with the usual form of beet knife and handled in large masses, as would be necessary in the conventional form of commercial-scale diffusion apparatus, would present excessive resistance to the flow of the flood liquid. For this reason special equipment may have to be designed for the extraction of the polysaccharides from jerusalem artichokes. This may involve the slicing equipment as well as the extraction apparatus, when the process is converted to a commercial scale. The new design might accommodate a different shape of slices and might involve a very different ratio of flood liquid to particles. In this connection it is interesting to compare the number and dimensions of the cossettes per cubic decimeter of displacement volume with the equivalents in respect of surface area for spheres and cubes. For example, if cossettes of the dimensions found by observer *A* (table 3) were to be replaced by uniform spheres of equal surface area per cubic decimeter of displacement volume, each sphere would have a radius of 0.1507 cm and 69,760 spheres would be required to displace 1 dm^3 of fluid and present 19,900 cm^2 of surface area. If cubes were substituted, each cube would measure 0.3015 cm on an edge and 36,490 cubes would be required to displace 1 dm^3 of fluid and present 19,900 cm^2 of surface area, the area indicated for 9,650 cossettes of the dimensions observed. A different shape of slices probably would involve specific surface areas and mean thicknesses of diffusion layers differing from those established in the experimental extractions. For this reason it is desirable to estimate also the mean thickness of the diffusion layers as they existed during the experimental extractions, in order to form an idea of the coefficient of diffusion of the polysaccharides under the experimental conditions.

8. THICKNESS OF DIFFUSION LAYERS

Obviously the layers must comprise films of stagnant liquid adherent upon the surfaces of the cossettes, films which at a given velocity of flux and a stable condition of packing change in composition only by mechanisms approximating diffusion in character, and films through which the polysaccharides within the cossettes must be transferred by diffusion. No wholly satisfactory method for their estimation has been devised but results that appear reasonable were obtained by the following procedure:

In each of two experiments (April 3 and July 23, 1925) a charge of cossettes was primed with flood liquid and immediately dropped into a sample receiver [2] and drained for 5 minutes. It is supposed that the difference between the calculated concentrations of the sap of the fresh cossettes, c'_s, and the observed concentrations of the apparent sap in the drained samples, c', respectively, was due solely to the replacement of the free fresh sap (from ruptured tissues) on the surfaces of the cossettes with an equal volume of flood liquid of

[2] J. Research NBS 15, 458 (1935) RP840; Ind. Eng. Chem. 27, 1273 (1935).

the concentration, c'', observed in the separated liquid. Thus, it is assumed that the volume of apparent sap in the drained sample was equal to the original volume of fresh sap in a charge of cossettes. Since this calculated total volume of fresh sap is v', the mixture (of concentration c') appearing as sap in the drained sample was composed of the volume, v''_1, of flood liquid film that had replaced the free fresh sap and the volume, $v'-v''_1$, of actual fresh sap from inside the tissues. Granting this, it is evident that from the resulting relation

$$(v'-v''_1)c'_s+v''_1c''=v'c', \qquad (3)$$

$$v''_1=\frac{c'_s-c'}{c'_s-c''}v'.$$

The indicated thickness of the flood liquid film is then expressed by the equation

$$L_2=\frac{v''_1}{A}10^{-1}, \qquad (4)$$

where L_2 stands for the thickness of the film in centimeters and A represents the surface area of the cossettes expressed in square meters. The numerical data are presented in table 4. It is assumed that once diffusion gradients have become established throughout the tissues of the cossettes, the thickness of the diffusion layers is $L=L_1+L_2$, where $L_1=t/2$ and t is the mean of t_1 and t_2.

TABLE 4.—*Data for estimation of diffusion-layer thickness, equation 4*

Item	Symbol	Unit	Experiment	
			April 3	July 23
Calculated total volume of fresh sap	v'	dm³/cell	1.0338	1.0136
Volume of film	v''_1	dm³/cell	.3847	.3545
Concentration of:				
Fresh sap	c'_s	g/dm³	133.80	156.01
Apparent sap	c'	g/dm³	121.40	134.84
Flood liquid	c''	g/dm³	100.48	95.48
Surface area	A	m²/cell	2.170	2.128
Thickness of film	L_2	cm	.0177	.0167
Do	Mean L_2	cm	0.017	
Thickness of tissue	Mean L_1	cm	0.069	
Thickness of layer	Mean L	cm	0.086	

Other assumptions which appear equally tenable yield values of the same order. For example, it can be supposed that the volume of free sap on the fresh cossettes was such as would contain the quantity of polysaccharides which during the respective experimental extraction apparently was washed out of the cossette mass, rather than diffused out. Suppose also that the whole of the free fresh sap was replaced in the drained sample by a volume of flood liquid which, when mixed with the remaining fresh sap inside the particles, would yield apparent sap of the observed concentration c'. In this case the indicated volume of the adhering flood liquid, divided by the area of the particles, yields the value $L_2=0.024$ cm as the thickness of the film, instead of $L_2=0.017$ cm as found above.

Here it may be anticipated that the relations between the concentrations of the apparent sap and the apparent flood liquid, and also the relations between their apparent rates of change, indicate that the mean thicknesses of the films during the extractions were nearer 0.024 cm. Thus the value of 0.017 cm is conservatively regarded as a minimum.

9. RELIABILITY OF ESTIMATES

Although, as a rule, the estimates of the same quantity by the three different observers, as presented in table 3, seem to be in practical agreement, it should be emphasized that most of these estimates involve indirect methods and that frequently the resulting data are presented in a larger number of significant digits than the precision of the observations can justify. This fact, however, does not invalidate the estimates as they will be used in subsequent papers of this series.

WASHINGTON, August 8, 1936.

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DIFFERENCE IN ATOMIC WEIGHT OF OXYGEN FROM AIR AND FROM WATER

By Edgar R. Smith and Harry Matheson

ABSTRACT

The hydrogen in ordinary water and that in water formed by burning commercial electrolytic hydrogen with atmospheric oxygen were brought to the same isotopic composition by equilibration with ammonia. The water containing atmospheric oxygen was then found to have a density greater by 8.6 ppm than that of the water containing aqueous oxygen. By this method of preparing two samples of water, which differ only with respect to the isotopic composition of their oxygen content, the use of electrolysis, with its attendant possibility of slight changes due to electrolytic fractionation, in the relative isotopic composition of the oxygen, is eliminated. The magnitude of the difference in density was also confirmed by an independent method. This involved the utilization of hydrogen and oxygen, having practically the same isotopic composition as in normal water, which are evolved after prolonged electrolysis until an equilibrium state is attained in a small commercial electrolyzer. A comparison of the water formed by burning together the electrolyzed hydrogen and atmospheric oxygen with the water formed by recombining the gases from the electrolyzer again yields the difference between atmospheric and aqueous oxygen. This difference is also obtained by comparison of the water formed by burning together tank hydrogen and atmospheric oxygen with the water formed by burning hydrogen from the same tank with oxygen from the electrolyzer. The measured difference in density corresponds to a difference of 0.0001_4 atomic weight unit between the atomic weights of atmospheric and aqueous oxygen.

A surprising difference between the isotopic composition of normal atmospheric oxygen and oxygen in normal water was discovered independently by Dole [1] and by Morita and Titani.[2] Dole first combined oxygen of the air with commercial hydrogen. Then, since the hydrogen of this water differed in atomic weight from the hydrogen of normal water, samples of both this water and normal water were electrolyzed by approximately the same fractional amount and both oxygens converted again to water with hydrogen from a single tank. In this way, the density of water made from tank hydrogen and oxygen originally from the air could be compared with the density of water made from the same tank hydrogen and oxygen originally from Lake Michigan water. As a result of two series of measurements, the difference in density between water made with oxygen of the air and water made with aqueous oxygen was found to be 6.0 ± 0.6 ppm. By fractional electrolysis of water, Morita and Titani prepared hydrogen having a deuterium content of less than 1 atom in 30,000. This light hydrogen was combined separately with oxygen of the air and with oxygen obtained from water by electrolyzing 95 percent of the initial water. The density of the water made with oxygen from the air was

[1] M. Dole, J. Am. Chem. Soc. **57**, 2731 (1935); **58**, 580 (1936); J. Chem. Phys. **4**, 268 (1936).
[2] N. Morita and T. Titani, Bul. Chem. Soc. Japan **11**, 36 and 414 (1936).

found to be greater by 8 ± 2 and 7 ± 1 ppm than that of the water made with aqueous oxygen. Greene and Voskuyl[3] have reported differences of 5.8 and 6.2 ppm in two experiments in which the densities of protium oxide with atmospheric oxygen and protium oxide with aqueous oxygen were compared. However, they did not publish the details of their technic.

The results of all these investigations, with the possible exception of those of Greene and Voskuyl, are not entirely free from the objection that the fractionation of the oxygen isotopes which occurs on electrolysis may possibly produce variations of 1 or 2 ppm in the densities of the resulting preparations if the conditions of electrolysis in the parallel experiments are not exactly the same. For this reason, and because a difference in density of 5 or more ppm between water with atmospheric oxygen and water with aqueous oxygen corresponds to a significant difference of 0.0001 or more in the atomic weights of atmospheric and aqueous oxygen, it seemed important to prepare for comparison, without resort to electrolysis, two samples of water, identical with respect to hydrogen, one with atmospheric oxygen and the other with aqueous oxygen.

For this direct comparison, about 500 ml of water was prepared by combining dried atmospheric oxygen with tank hydrogen.[4] The density of the water thus prepared was 1.2 ppm greater than that of normal water. This water was then saturated and desaturated successively four times with dried ammonia.[5] The same volume of normal water, having the Potomac River as its source, was then saturated and desaturated successively twice with the same tank ammonia.[6] By this treatment the hydrogen of both waters was brought to the same isotopic composition, and any difference in density would be due to a difference in the isotopic composition of atmospheric and aqueous oxygen. After purification, the water containing atmospheric oxygen was found to have a density greater by 8.5 ppm at 25° C than that of the water containing aqueous oxygen. The density measurements were made by the twin quartz pycnometer method which has been described in detail.[7 8] Following this first determination, both waters were subjected to two more successive saturations and desaturations and, after purification, were found to differ again in the same way in density by 8.7 ppm. The average of the two results is 8.6 ppm. The use of anhydrous ammonia as an equilibrating agent for the hydrogen of water is rapid and effective, as was first shown by Lewis,[9] and in the present case permits the direct measurement of the difference in density due to the difference in oxygen alone, and eliminates electrolytic fractionation. The agreement of the two determinations shows that equilibrium with the ammonia had been attained. In using this method it is assumed, of course, that the exchange of deuterium and hydrogen

[3] C. H. Greene and R. J. Voskuyl, J. Am. Chem. Soc. **58**, 693 (1936)

[4] M. Dole, Loc. cit., has shown that no measurable fractionation of the oxygen isotopes occurs during combustion.

[5] In some unpublished work done in this laboratory it has been found that after ammonia is absorbed by water having a larger proportion of deuterium than normal, until the total volume is approximately doubled while the container is immersed in a cooling mixture, and then the ammonia is expelled, the deuterium content of the water is reduced by about 45 percent each time the cycle is performed. This is the procedure referred to as saturation and desaturation with ammonia.

[6] Previous work had shown that the hydrogen of this ammonia and of ordinary water have practically the same isotopic composition.

[7] E. W. Washburn and E. R. Smith, BS J. Research **12**, 305 (1934) RP656.

[8] E. R. Smith and M. Wojciechowski, Rocznïki Chem. **16**, 104 (1936); Bul. int. acad. polonaise (A) March (1936)

[9] G. N. Lewis, J. Am. Chem. Soc. **55**, 3502 (1933).

between ammonia and water is independent of the kind of oxygen present.

An interesting, although not very accurate, confirmation of the density difference in question was obtained in the following way. A commercial electrolyzer of the filter-press type, having 56 nickel-plated cast-iron cells in series, and a capacity of 16 liters, was filled with alkaline solution from the large commercial cells of the Southern Oxygen Company, South Washington, Va. The solution was electrolyzed continuously, on a 24-hour day basis, with the addition of normal water in 250-ml portions to keep practically constant the level in the electrolyzer, until the water formed by recombining the electrolyzed gases did not differ in density from normal water by more than 1 ppm. In this state the gases evolved have practically the same isotopic composition as in the normal water added to the cell,[10] so that the hydrogen from the electrolyzer, H^E, is practically identical with the hydrogen from normal water, H^W, and oxygen from the electrolyzer, O^E, is almost the same as the oxygen in normal water, O^W, i. e. $H^E \cong H^W$ and $O^E \cong O^W$. At this stage, hydrogen from the electrolyzer was burned with dried atmospheric oxygen, O^A, to form water which may be designated as $H^E{}_2O^A$. The combustions were made with a gas burner inclosed in a flame hood connected to a condenser. After purification, the density of this water was found to be greater than that of $H^E{}_2O^E$ by 9.7 and 9.6 ppm in two determinations with intervening distillation of both preparations. This difference should approximate that between two samples of water, one containing atmospheric oxygen, the other aqueous oxygen, and both with the same hydrogen.

Hydrogen from a certain tank was also burned with atmospheric oxygen to form $H^T{}_2O^A$, and with oxygen from the electrolyzer to form $H^T{}_2O^E$. The density of $H^TO_2{}^A$ was found to be greater than that of $H^T{}_2O^E$ by 7.4 and 7.9 ppm in two determinations with intervening distillation of both preparations. This difference should also approximate the value under investigation. The average of the differences, 9.7, 9.6, 7.4 and 7.9 ppm, found in the work with the electrolyzer filled with "equilibrium" water is 8.7 ppm. The close agreement between this average and the more precisely measured value of 8.6 ppm obtained by the direct method of equilibrating the hydrogens is obviously fortuitous, since the level of electrolyte in the electrolyzer can be kept only approximately constant and small fluctuations in the isotopic composition of the gases evolved is unavoidable. However, the order of magnitude of the difference is confirmed, and the value of 8.6 ppm is believed to be accurate to within 1 ppm.

All results reported up to the present time are summarized in table 1. The discrepancy of about 2 ppm between the values reported by Dole, and by Greene and Voskuyl; and those reported by Morita and Titani, and in the present work, is apparently greater than the experimental error involved in the determination of density. It is also greater than the variation to be expected in normal water from different locations, since even the difference between water from the ocean and normal water from different places is only about

[10] This is an assumption, since the possibility remains that one, e. g., hydrogen, is lighter and the other, e. g., oxygen, is heavier than normal, the combination yielding water of normal density.

2 ppm.[11] [12] [13] Lake Michigan water was found by Greene and Voskuyl to have the same density as Cambridge, Massachusetts, tap water, and the difference in density between Atlantic Ocean water and Cambridge water is the same as between Atlantic Ocean water and Potomac River water. These results show indirectly that Lake Michigan water is the same as Potomac River water. The average of the mean values reported by all investigators is about 7 ppm, and in view of the fact that the value found in this investigation was obtained by a more direct method, it may be best at the present time to adopt a value of 8.0 ppm as probably correct within 1 ppm. This difference in density is equivalent to a difference in the atomic weight of atmospheric oxygen and normal aqueous oxygen of 0.0001_4 atomic weight unit.

TABLE 1.—*Increase in density (Δd) of water with atmospheric oxygen over water with aqueous oxygen*

Investigator	Δd	Average
	ppm	ppm
Dole	6.0, 6.0	6.0
Morita and Titani	(8.0), 7.0	7.0
Greene and Voskuyl	5.8, 6.2	6.0
Smith and Matheson	8.5, 8.7	8.6

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WASHINGTON, August 15, 1936.

[11] E. S. Gilfillan, J. Am. Chem. Soc. **56**, 406 (1934).
[12] C. H. Greene and R. J. Voskuyl, J. Am. Chem. Soc. **56**, 1649 (1934).
[13] E. W. Washburn and E. R. Smith, BS J. Research **12**, 305 (1934) RP656.